



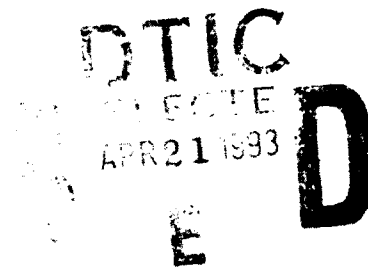
**SPECIFIC IMPULSE CALCULATIONS OF HIGH ENERGY
DENSITY SOLID CRYOGENIC ROCKET PROPELLANTS
1: ATOMS IN SOLID H₂**

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April 1993

Final Report



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FOREWORD

This final report was submitted by the OLAC PL/RKFE Branch, at the Phillips Laboratory, Edwards AFB CA 93524-7680. OLAC PL Project Manager was Dr Patrick G. Carrick

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13. ABSTRACT (MAXIMUM 200 WORDS) Specific impulse calculations for a wide range of input concentrations are reported for atomic additives to solid hydrogen, combusted with liquid oxygen. These specific impulse values are presented in the form of 3D contour plots that reveal information about an entire region of interest. The output product species are also presented in this manner. These plots can be used to determine the optimum performance of any particular additive concentration and provide insight into how the performance level changes with concentration of the additive, temperature in the chamber, and exhaust product species.				
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INTRODUCTION

The High Energy Density Matter (HEDM) program was initiated at the Air Force Rocket Propulsion Laboratory (now the Phillips Laboratory, Propulsion Directorate) in 1987 to investigate potential new high energy propellants for advanced rockets and missiles (1). One major focus of this program is to determine the feasibility of trapping energetic atoms or small molecules in cryogenic solids, such as solid hydrogen and solid oxygen. A program to study this idea was conducted by the National Bureau of Standards from 1956 to 1959 and concluded that, although free radicals could make great improvements in rocket performance, the difficulties associated with production, storage, and maximum concentrations preclude their use as fuels (2). Improvements in technology and theory since the NBS study provided impetus for a reinvestigation of the use of "free radical" additives to fuels, giving rise to the HEDM program.

A common figure of merit for a propellant is the specific impulse, I_{sp} , measured in "lb sec/lb", or more typically in "sec" (2,3,4). The I_{sp} can be used to compare the performance of a series of propellants, as long as all the assumed conditions remain constant. Such comparisons can point to areas of research that can result in the best increases in rocket performance. Calculations of the I_{sp} for atoms and small molecules stored at various concentrations in solid cryogenic hydrogen have been completed and are reported here.

Since the specific impulse depends on both the energy content and the mass of the propellant (4), only low mass atoms and small molecules can be expected to result in improvements in rocket propulsion. A survey of the combustion energies of the elements (with oxygen) from hydrogen to argon indicate which elements might lead to significant improvements (1) in specific impulse: beryllium, boron, lithium, carbon, aluminum, silicon, and magnesium, in order of decreasing combustion energy. To accurately determine the properties of these elements with respect to rocket propulsion, calculations of the specific impulse under set conditions are necessary.

SPECIFIC IMPULSE CALCULATIONS

Calculations of the specific impulse (I_{sp}) of atom and molecule additive hydrogen/oxygen systems were conducted using the AFAL (Air Force Astronautics Laboratory, recently renamed the Phillips Laboratory) Theoretical I_{sp} Program, Micro Version, by Beckman and Acree (5). This program requires input data consisting of the molar percentage of the additive, heat of formation of the additive, rocket chamber pressure and exhaust pressure. The fraction of hydrogen and oxygen in the system and the temperature of the combustion chamber, throat, and exhaust can be varied to maximize the I_{sp} for the entire system. The rocket chamber pressure and exhaust pressure can be fixed to specific values to give a consistent comparison among the various additives. These values were fixed to 1000 and 14.696 psi, respectively. The program also has the capability of calculating an entire grid of data values for a range of input concentration values. This grid calculation can be used to plot a 3D surface or a contour plot of the specific impulse, temperature, and chemical composition of the entire system as calculated under the particular values for chamber and exhaust pressures.

The heats of formation of the gaseous atoms from elements in their standard states were obtained from the *JANAF* tables (6), the *Handbook of Chemistry and Physics* (7) and the CODATA (Committee on Data for Science and Technology) values given therein. The heat of formation for each of the atoms considered in this study are given in Table 1. The CODATA values were used for all the atoms.

Initially the I_{sp} values were calculated for gas phase atoms as a mole percentage in gaseous hydrogen. The majority of the calculations assume gas phase atoms as a mole percentage in solid hydrogen. The "true" heats of formation for a particular concentration of an atomic additive in solid hydrogen will depend on the interaction between the isolated atom and the solid hydrogen host matrix. The strength of these interactions are not known in general, but should be relatively small. Therefore, the atomic heats of formation should provide a close approximation to the "true" heats of formation of these species in solid hydrogen.

The heat of formation for solid hydrogen was determined by adding the heat of fusion of hydrogen (plus a small heat capacity for heating the liquid to its boiling point) to the heat of formation for liquid hydrogen. It turns out that this adds only 0.05 Kcal/mol to the ΔH_f value for liquid hydrogen, giving a value of -2.210 Kcal/mol for solid hydrogen at 4K. The density of solid hydrogen also increases to 0.08 grams/cc, compared to 0.07 grams/cc for liquid hydrogen.

The calculations of the I_{sp} program were tested by comparing the results with I_{sp} values previously reported. Under the same operating conditions, the program gave the same I_{sp} values for several systems reported by Rockwell International ("Theoretical Performance of Rocket Propellant Combinations" wall chart, from Rocketdyne Division). The program was also run under the same conditions reported for the Space Shuttle Main Engine (SSME): 3260 psi chamber pressure, epsilon of 77.5, O/F weight ratio of 6:1, with LOX/LH₂, and resulted in an I_{sp} value of 465.4 sec, compared with the reported measured value of 453.5 sec. However, the specific impulse values reported here should only be used for comparing like systems, since the heats of formation for the additive/ SH_2 material will be slightly different from the values used here.

TABLE 1. Heats of Formation (Kcal/mol) Used in I_{sp} Calculation

Atom	JANAF ⁶	CRC ⁷	CO-DATA ⁸	ΔH_f used
H	53.103 \pm .001	52.102 \pm .001	52.103 \pm .001	52.10
Li	38.07 \pm .24	38.6 \pm .4	38.07 \pm .24	38.1
Be	77.44 \pm 1.2	77.5 \pm 1.5	77.4 \pm 1.2	77.4
B	133.8 \pm 2.9	139 \pm 3	135.0 \pm 1.2	135.0
C	171.29 \pm .11	171.29 \pm .11	171.29 \pm .11	171.3
N	112.97 \pm .10	112.97 \pm .10	112.97 \pm .10	113.0
Mg	35.16 \pm .19	35.0 \pm .3	35.16 \pm .19	35.2
Al	78.8 \pm 1.0	78.8 \pm 1.0	78.87 \pm .96	78.8
H ₂ (s)				-2.210

SPECIFIC IMPULSE OF ATOMS IN SOLID HYDROGEN

Recent studies conducted as part of the HEDM program have investigated the limitations of trapping atoms in cryogenic solids (9). Reference 9 concluded that concentrations of up to 10 % may be possible, depending on the crystal structure and the trapping site that the atom occupies. At the higher concentration levels, a certain concentration of dimers and higher order clusters is inevitable. However, for concentrations of 2 %, the atoms comprise about 90 % of the trapped species, and for 5 %, the atoms comprise at least 50 % of the trapped species. The maximum mole fraction for a face-centered cubic (fcc) crystal is 7.7 % for Li atoms, according to the model in Reference 9. Therefore, a loading of 5 % for atoms in solid hydrogen seems reasonable, with higher percentages possible.

Specific impulse calculations, under the conditions defined above and conducted for 5 mole percent of "light" atoms in gaseous and cryogenic solid hydrogen, are presented in Table 2. The values for pure solid hydrogen and gaseous hydrogen are listed for comparison. In addition, the I_{sp} value for liquid hydrogen under these conditions is 390 seconds, essentially the same as for solid hydrogen, as expected due to the small difference in the heat of formation between liquid and solid hydrogen. Table 2 also contains the increase in specific impulses for each additive in solid hydrogen over the value for liquid hydrogen/liquid oxygen (390 seconds). As can be seen from this comparison, increases of over 20 % can be obtained.

The percent increase in the I_{sp} of the 5 mole percent additives in solid hydrogen vs gaseous hydrogen (10) vary between about 4 % and 10 %. Since only the ΔH_f for hydrogen changes between the gas and solid calculations, the combustion conditions must vary in different ways with the various additives. One important variable that can change is the temperature in the combustion chamber, which in turn alters the thermochemical conditions in the chamber. The chemistry and the temperature conditions for these additives will be explored in a later section.

TABLE 2. I_{sp} of Atoms for 5 Mole Percent in Hydrogen

Species	I_{sp} 5% w/ SH_2 (sec)	I_{sp} 5% w/ gH_2 (sec)	Delta g-s (sec)	Delta g-s (%)	Increase of solid over $LH_2 \backslash LOX$ (sec) %	
H_2	(389)	(403)	14	3.5	-14	-4
H	407	426	19	4.5	17	4
Li	401	426	25	5.9	11	3
Be	451	492	41	8.3	61	16
B	470	501	31	6.2	80	21
C	469	518	49	9.5	79	20
N	414	435	21	4.8	24	6
Mg	398	415	17	4.1	8	2
Al	425	452	27	6.0	35	9

SPECIFIC IMPULSE CONTOUR CALCULATIONS

Calculations of the entire set of conditions for a mix of propellants can be used to study the variation in specific impulse over the full range of additives. The matrix of data, which consists of a range of fuel, oxidizer, I_{sp} , and other relevant parameters, can be analyzed by plotting a 3D contour plot (essentially a topological map) of the additive vs the oxidizer vs the specific impulse. Such plots contain a wealth of information, showing the I_{sp} for no additive (along the X axis), the I_{sp} for the additive without oxidizer (which would be a monopropellant, along the Y axis), and the optimum I_{sp} for any given additive amount. Calculations of this type were completed for the atoms of interest in this study and are presented in Figures 1 through 8. The top graph (labeled a) in each figure shows the full range of interesting additive amounts for oxidizer amounts up to 25 mole percent. The bottom graph (labeled b) shows the range of additives that seems practical, as determined by the study discussed above (9).

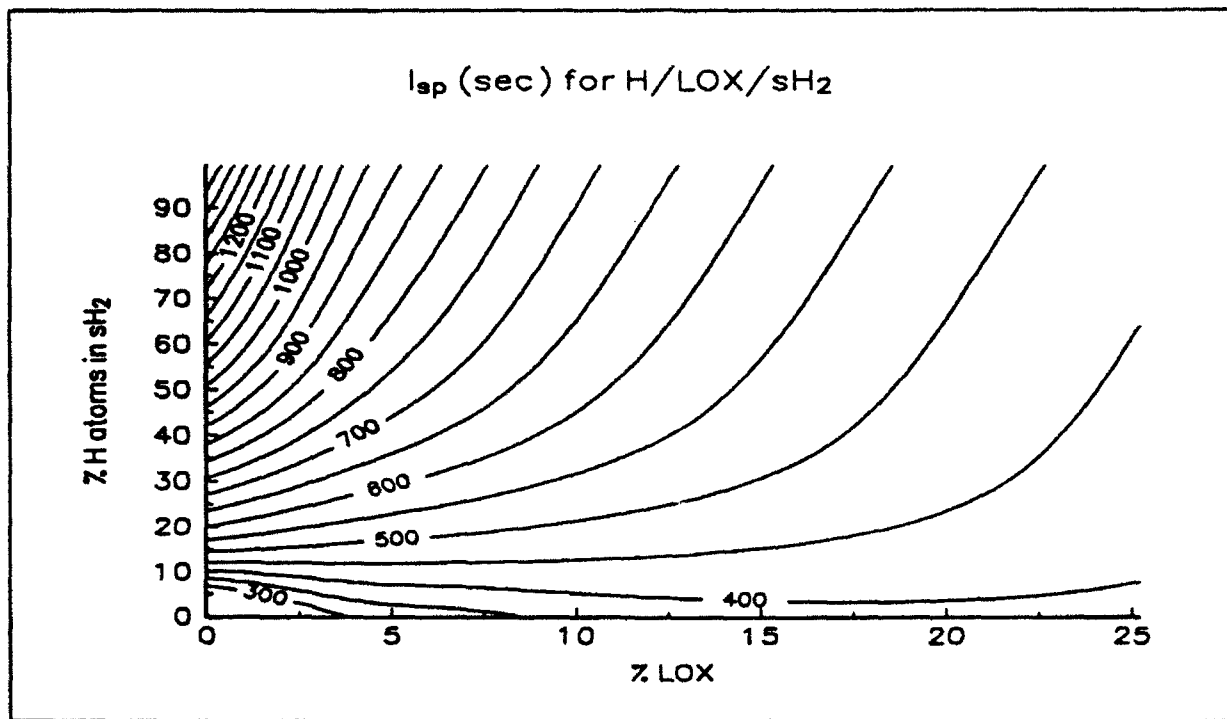


FIGURE 1a
Specific Impulse Contour Plot for Hydrogen Atoms

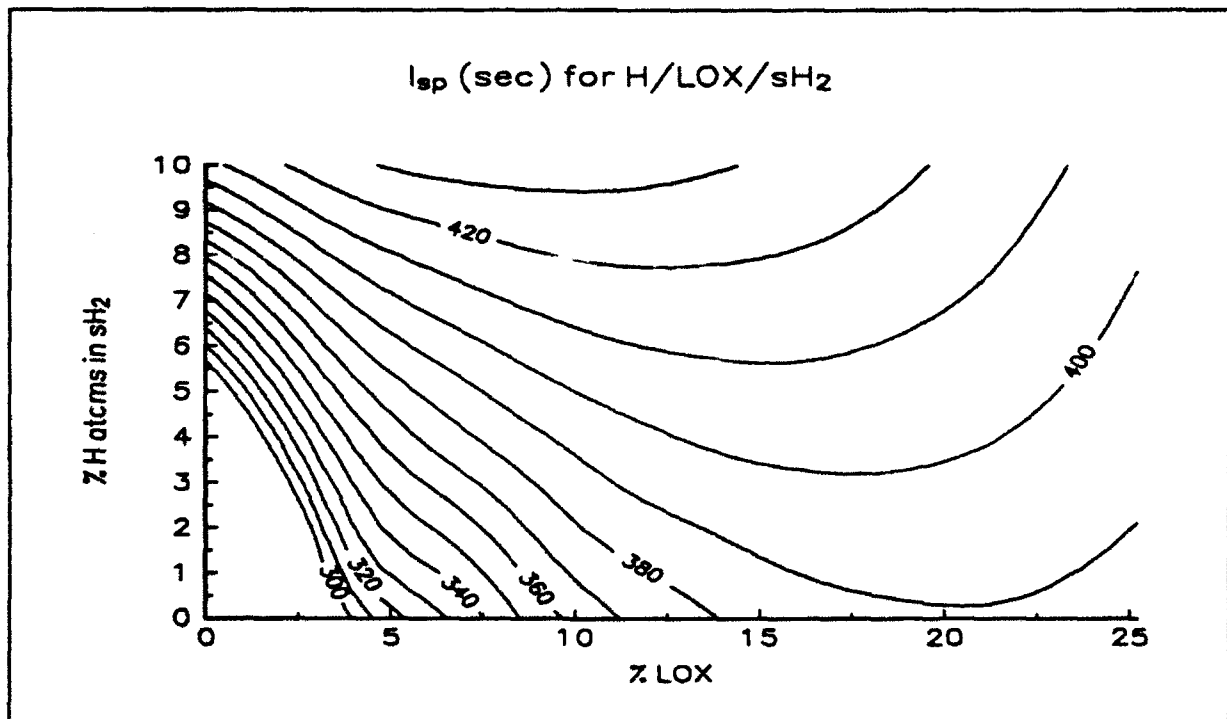


FIGURE 1b
Expanded Specific Impulse Contour Plot for Hydrogen Atoms

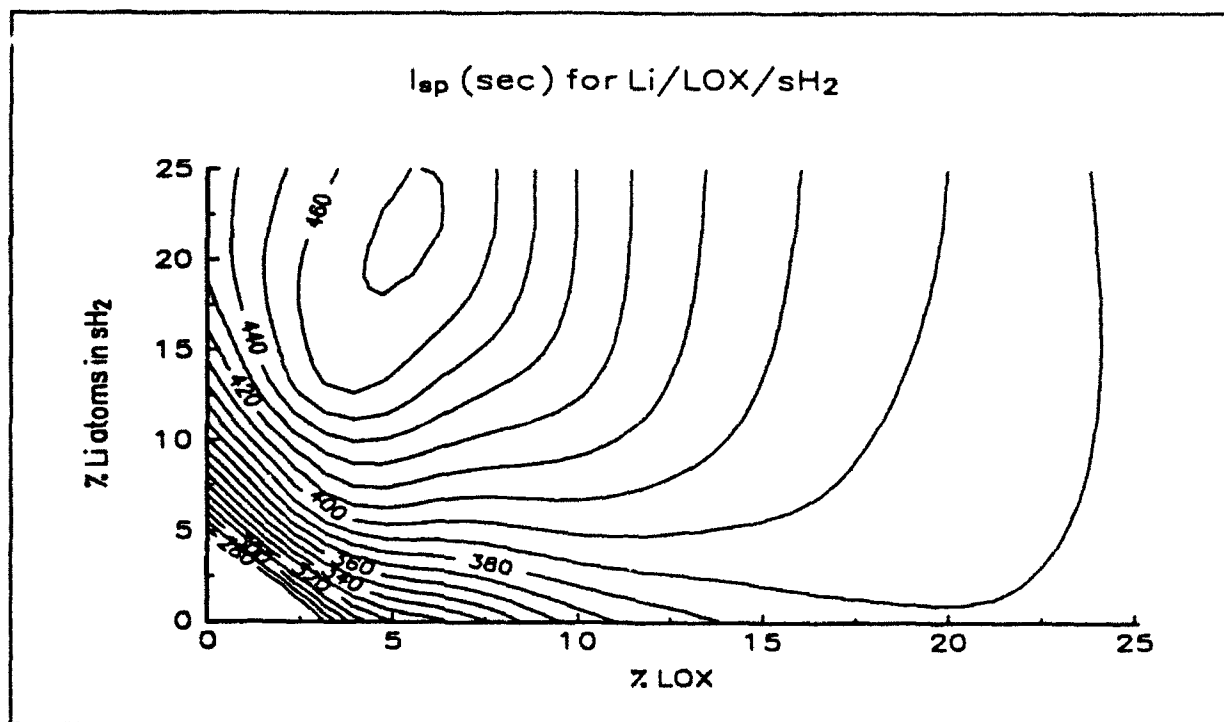


FIGURE 2a
Specific Impulse Contour Plot for Lithium Atoms

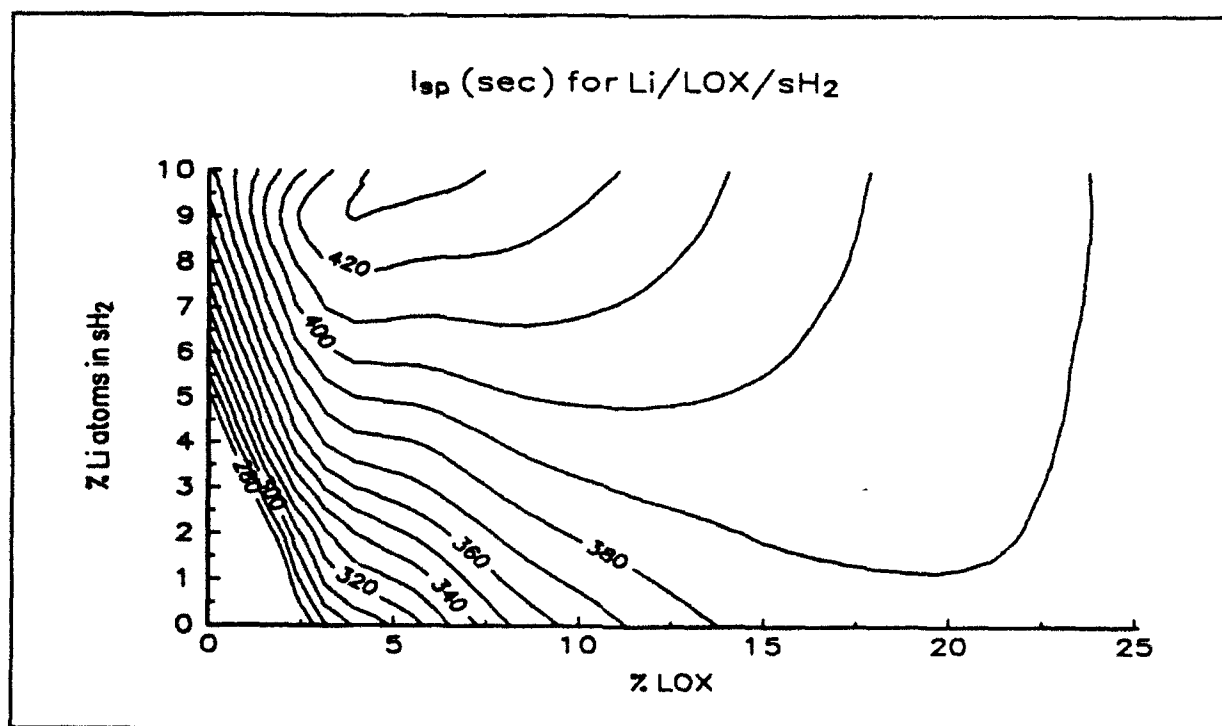


FIGURE 2b
Expanded Specific Impulse Contour Plot for Lithium Atoms

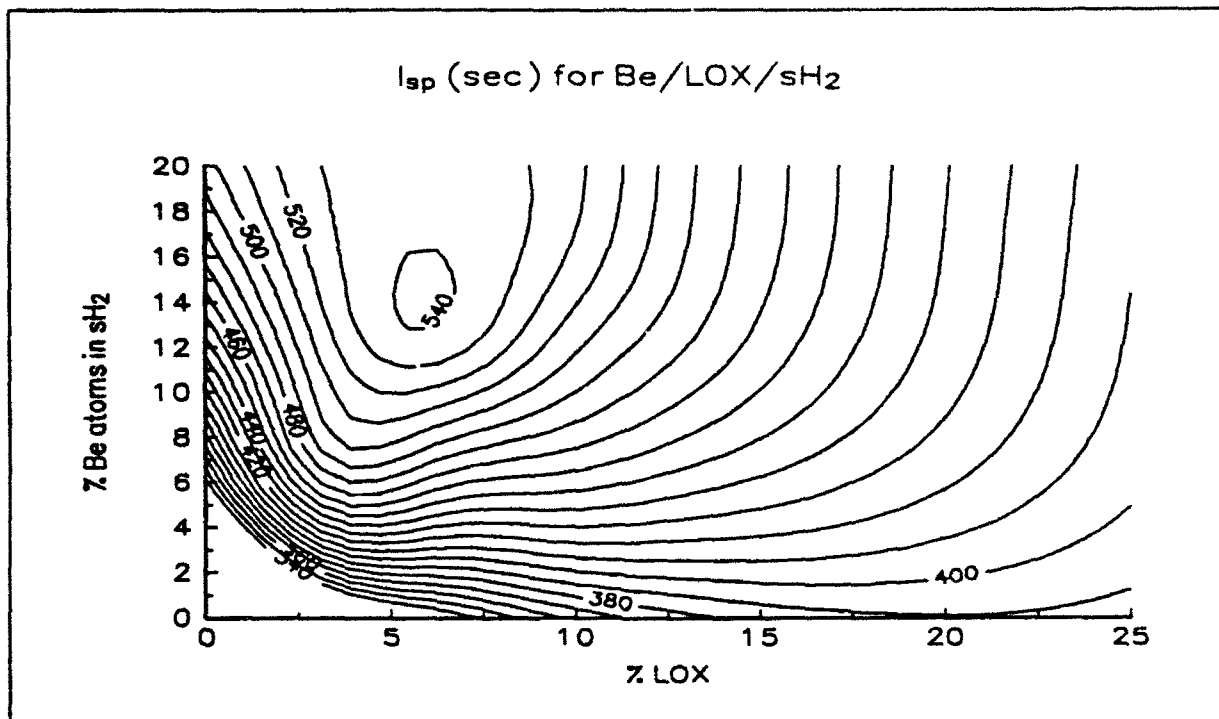


FIGURE 3a
Specific Impulse Contour Plot for Beryllium Atoms

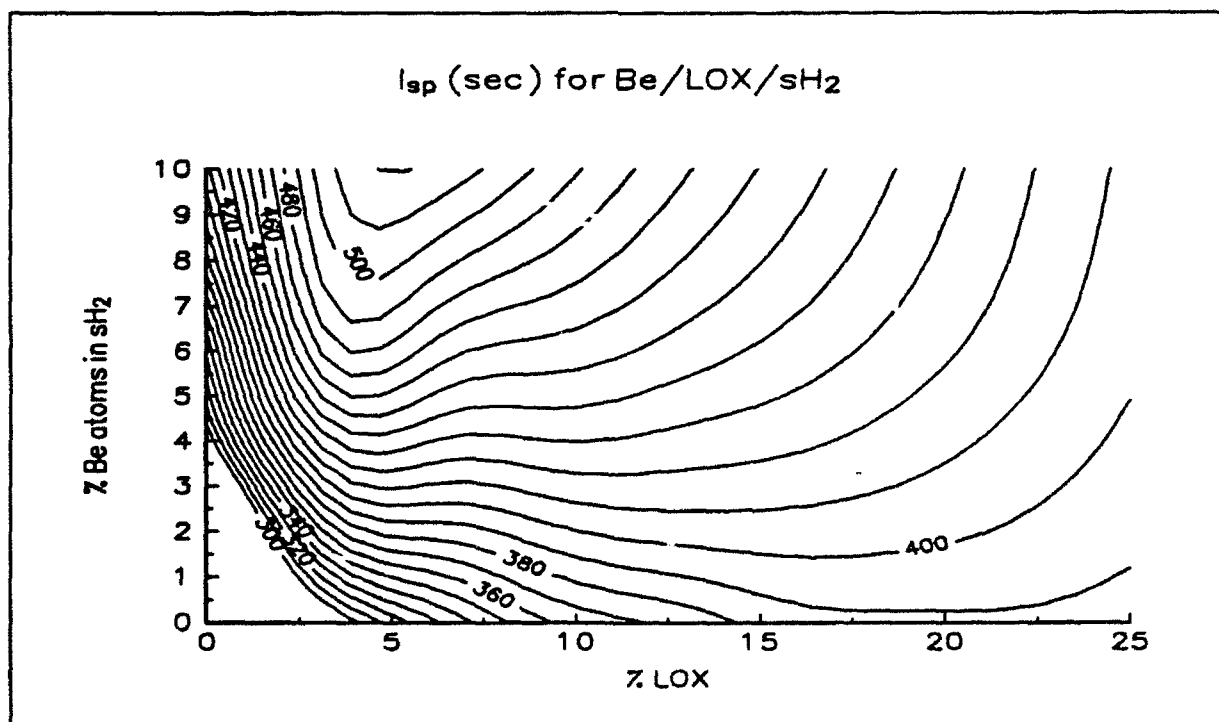


FIGURE 3b
Expanded Specific Impulse Contour Plot for Beryllium Atoms

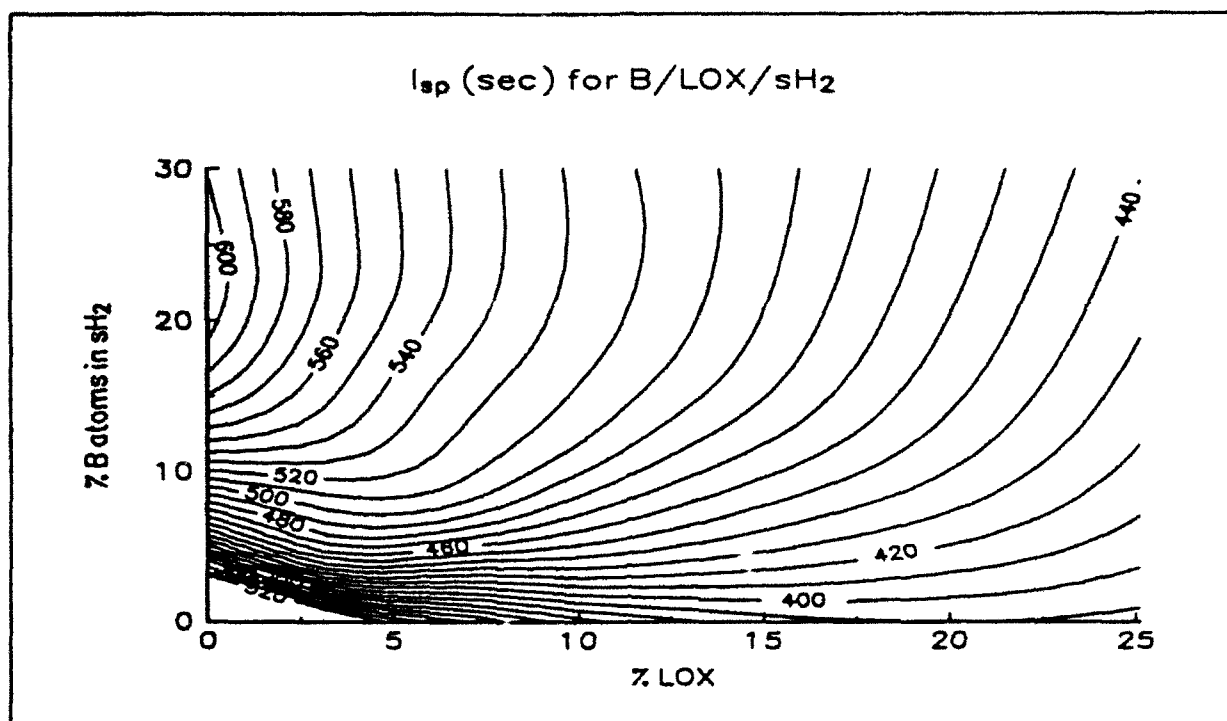


FIGURE 4a
Specific Impulse Contour Plot for Boron Atoms

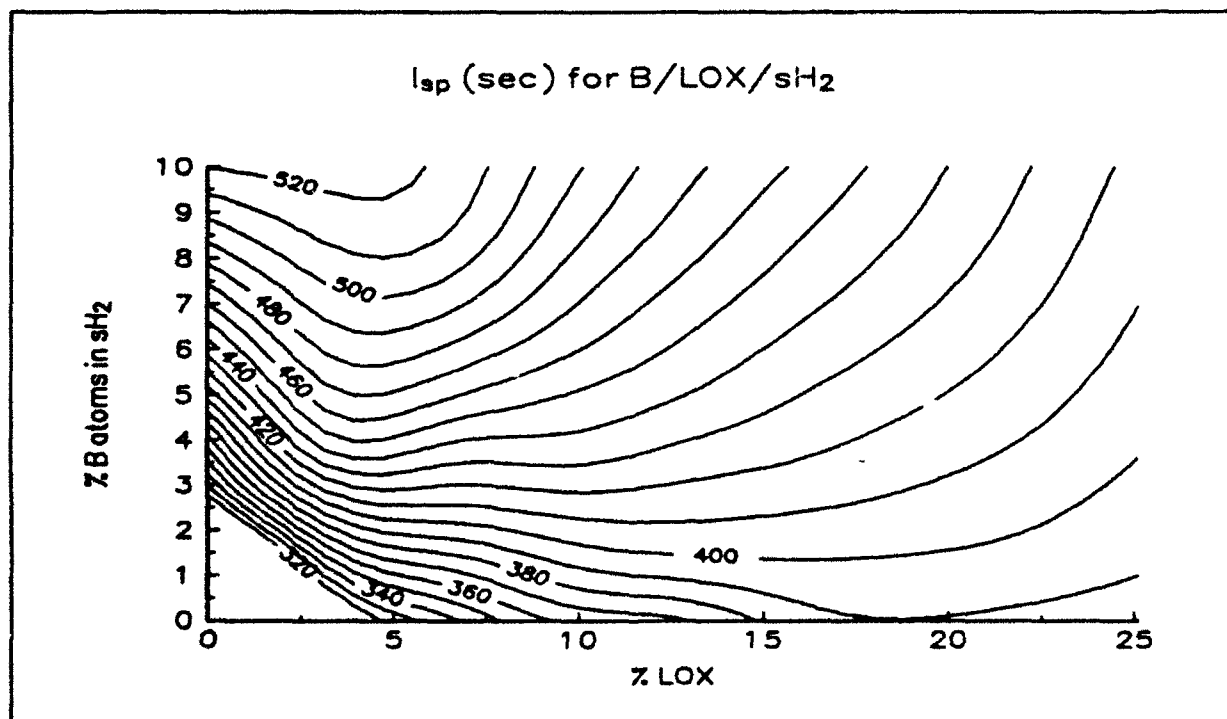


FIGURE 4b
Expanded Specific Impulse Contour Plot for Boron Atoms

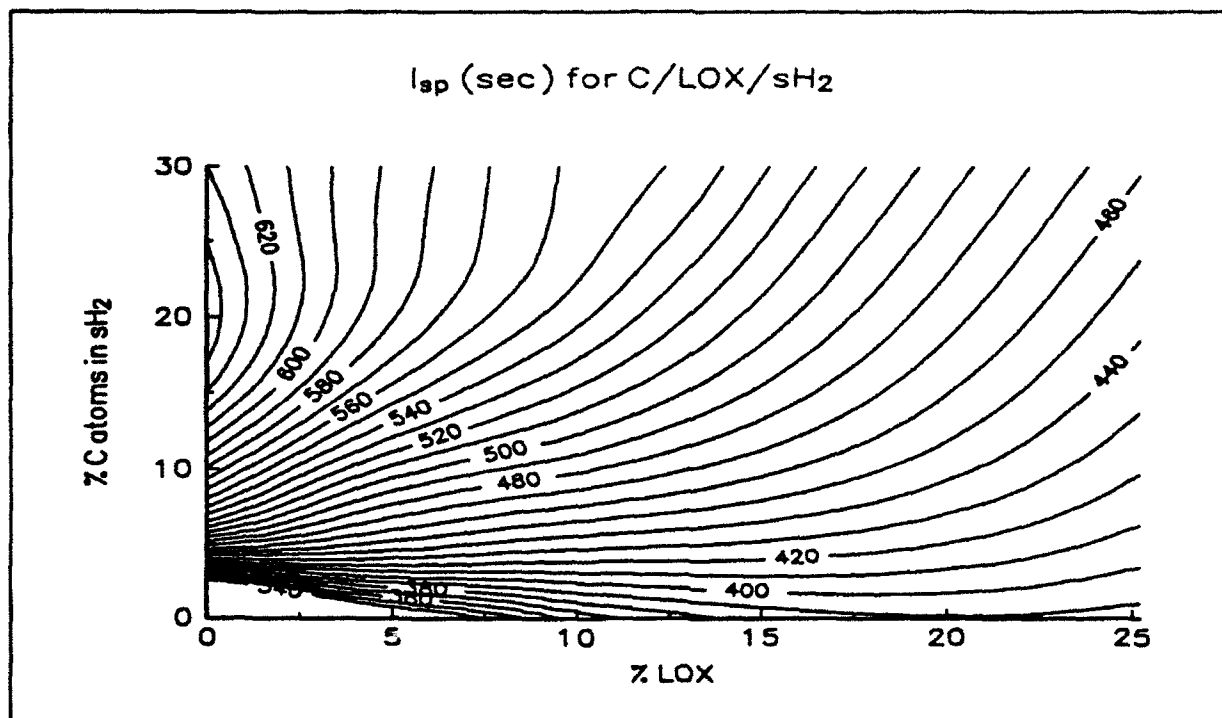


FIGURE 5a
Specific Impulse Contour Plot for Carbon Atoms

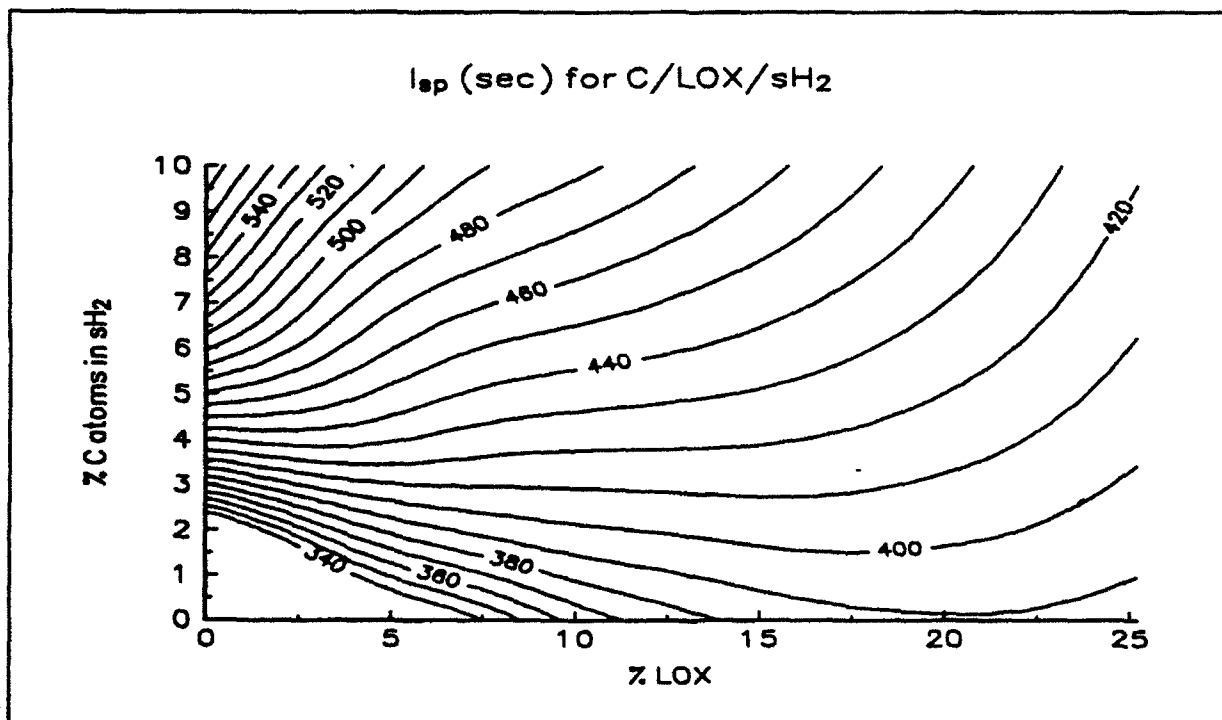


FIGURE 5b
Expanded Specific Impulse Contour Plot for Carbon Atoms

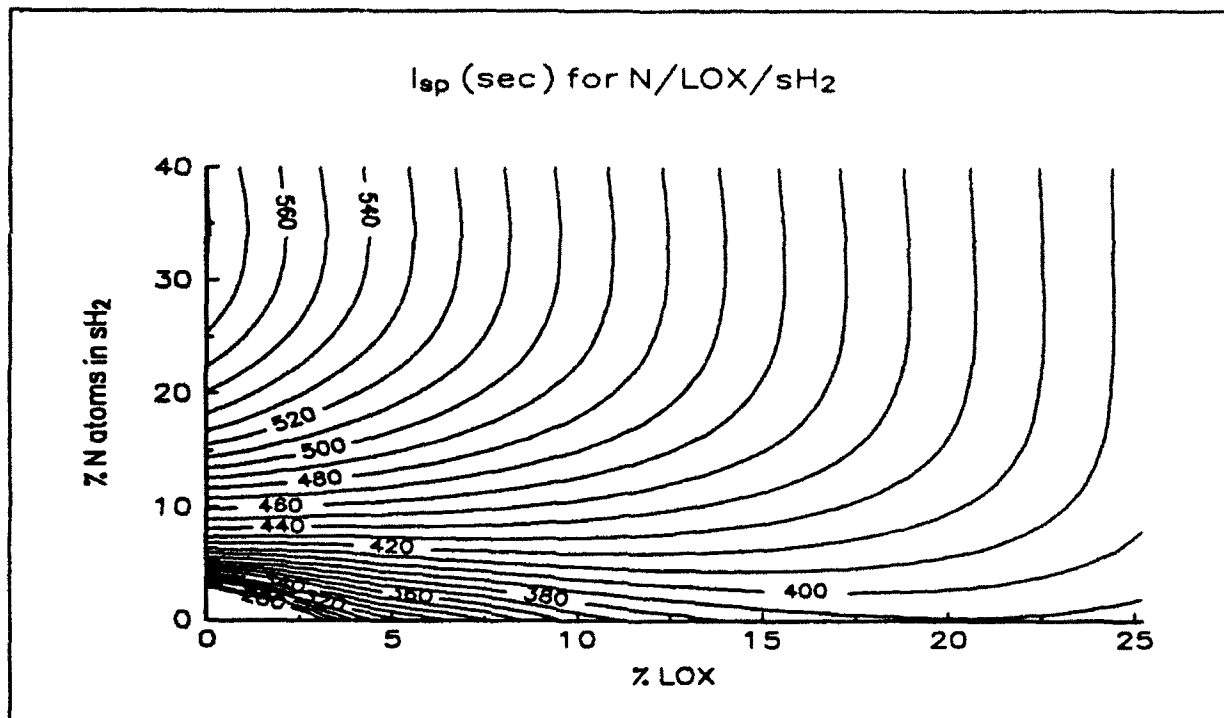


FIGURE 6a
Specific Impulse Contour Plot for Nitrogen Atoms

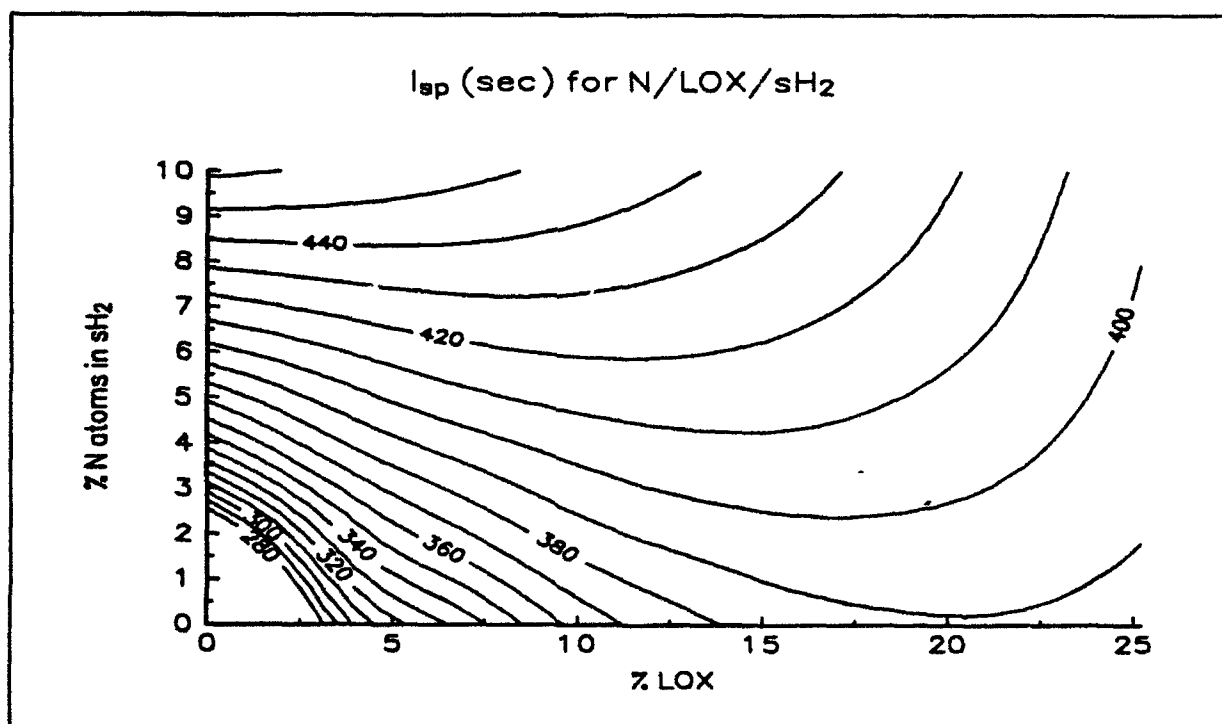


FIGURE 6b
Expanded Specific Impulse Contour Plot for Nitrogen Atoms

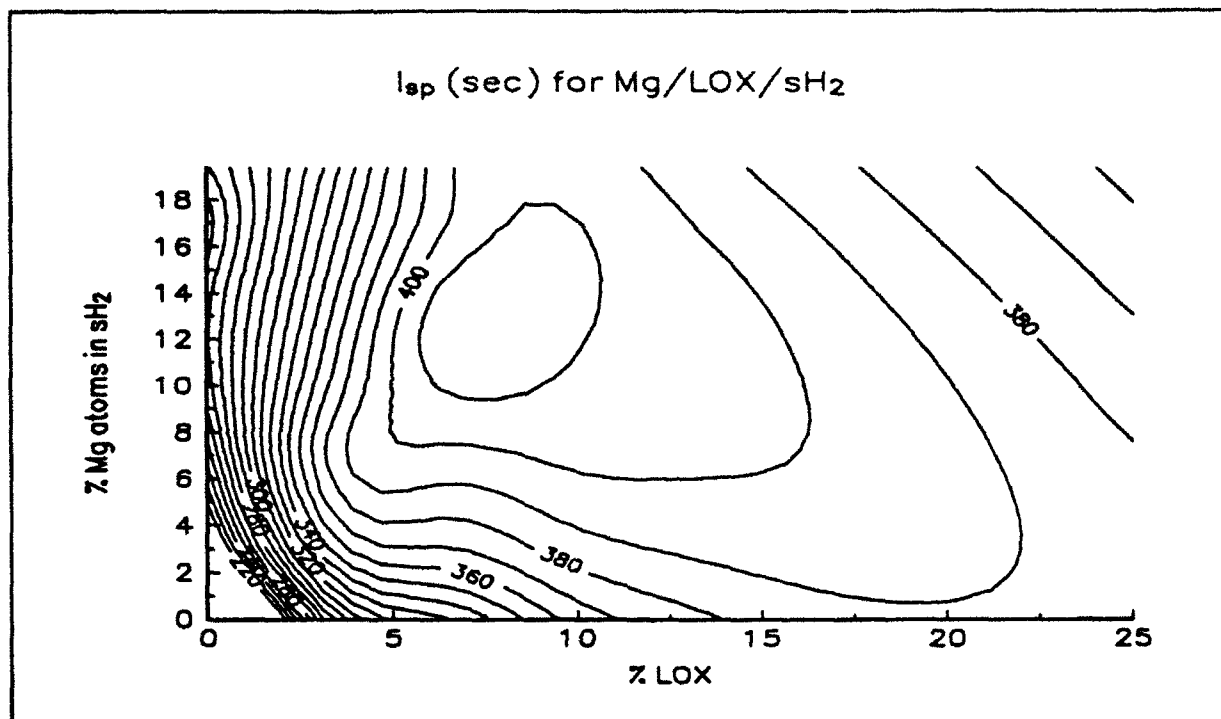


FIGURE 7a
Specific Impulse Contour Plot for Magnesium Atoms

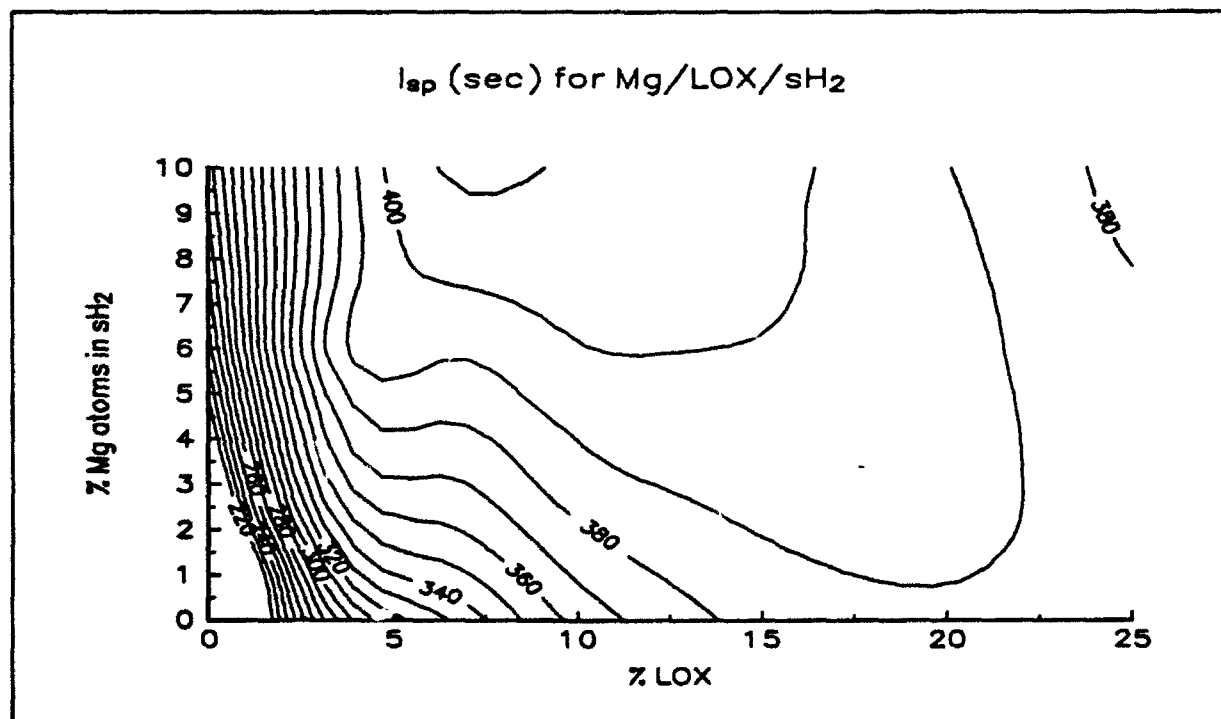


FIGURE 7b
Expanded Specific Impulse Contour Plot for Magnesium Atoms

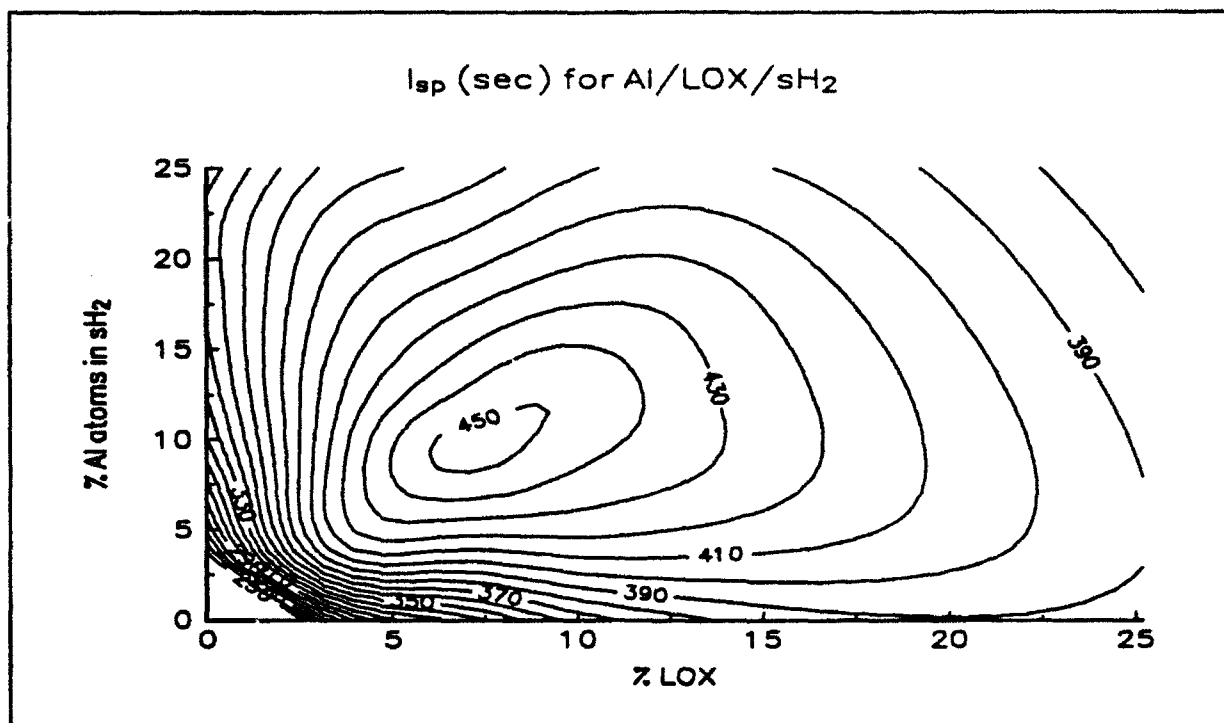


FIGURE 8a
Specific Impulse Contour Plot for Aluminum

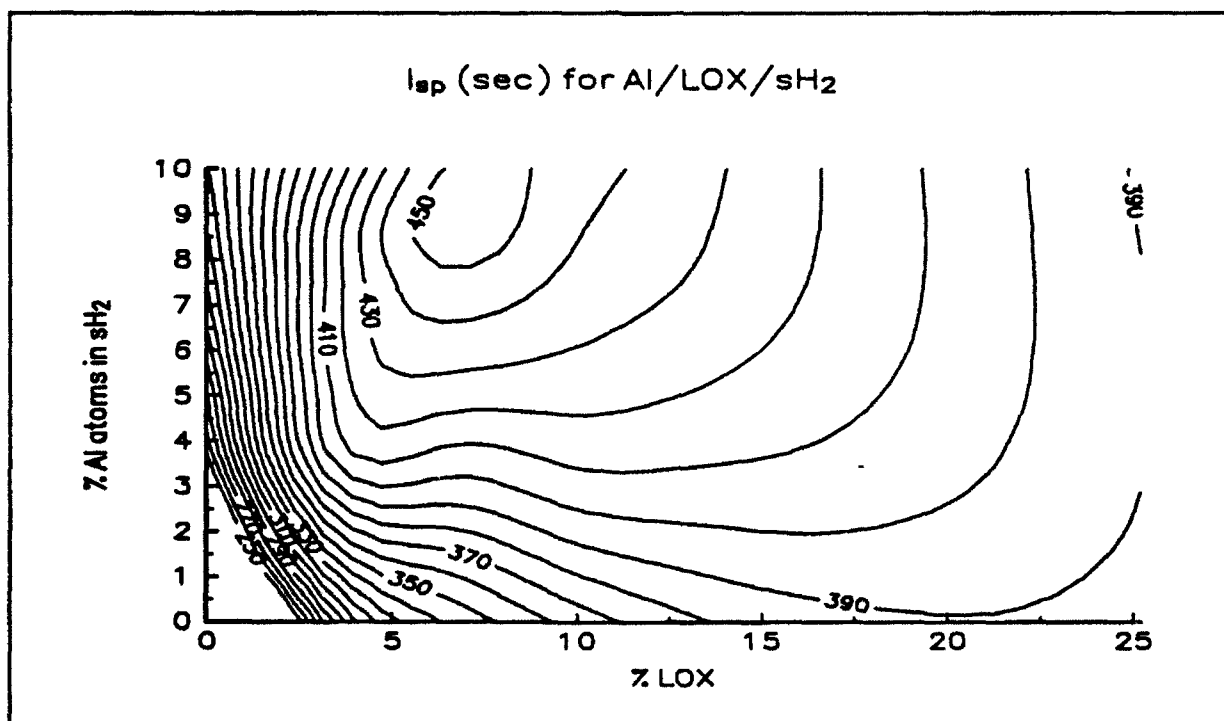


FIGURE 8b
Expanded Specific Impulse Contour Plot for Aluminum

The contour for hydrogen atoms in solid hydrogen (Fig. 1, a and b) shows a slow increase in I_{sp} from 0 to 10 mole percent, but large gains for amounts of H/sH₂ over 10% and without LOX. If a propellant of 100% hydrogen atoms could be obtained (10), the I_{sp} would increase to over 1400 seconds. However, for the quantity of hydrogen atoms that can be trapped in solid hydrogen at low temperature and pressures less than 100 atmospheres, the specific impulse gains are moderate at best (12). Note that, for hydrogen atom quantities over 12%, adding liquid oxygen actually reduces the specific impulse.

The 0 to 10 mole percent contour (Fig. 2b) for lithium atoms shows about the same gains as obtained with hydrogen. The maximum I_{sp} gain (Fig. 2a) results from a lithium concentration of over 20%, which is probably unobtainable.

The I_{sp} gains for beryllium are substantially greater than for either hydrogen atoms or lithium atoms. The I_{sp} increases rapidly over the 1 to 10% range (Fig. 3 b) of interest. The optimum addition of oxygen decreases from 20% to about 4% over this range. The optimum I_{sp} (Fig. 3a) is still over 10%, but most of the gain results from lower amounts. Unfortunately, beryllium and beryllium oxides are extremely toxic (4), and, therefore, probably not useful as a "near-Earth" rocket propellant. However, the use of beryllium propellants for deep space applications may be feasible.

The gains in I_{sp} for boron atoms in solid hydrogen show the same rapid increase at relatively low concentrations (Fig. 4b). As with beryllium, the optimum oxidizer amount decreases from 20% to about 4% and the largest gains in I_{sp} result from additions up to 10% of boron atoms. At just over 10%, addition of oxygen becomes unfavorable for optimum I_{sp} (Fig. 4a), which would provide "monopropellant" capabilities. A boron atom concentration of 7% results in a 100 second I_{sp} increase over liquid hydrogen/liquid oxygen under these conditions. Even at the 5% level, boron atoms in solid hydrogen and without LOX could give a 15 second I_{sp} increase over LOX/LH₂.

The specific impulse gains for carbon are quite similar to boron. Once again, there is a rapid increase from the 1 to 10% additive range (Fig. 5b). However, carbon atoms in solid hydrogen become a "monopropellant" at much lower concentrations: the "turn-over" point is at about 4.5% carbon atoms. At 7% carbon atoms in solid hydrogen, an I_{sp} increase of over 130 seconds is possible as a "monopropellant."

Nitrogen atoms in solid hydrogen result in contour plots similar in form to carbon atoms, except for lower gains at the 1 to 10% level (Fig. 6b). The turn-over point is about 9% and therefore oxygen is required for optimum specific impulse at the 5 or 7% level.

Magnesium atoms show the smallest increase in I_{sp} over 1 to 10% concentration range (Fig. 7b). An increase of just 13 seconds results from a 7% concentration of magnesium atoms. Even the optimum I_{sp} (Fig. 7a) is only about 25 seconds greater than LOX/LH₂. Therefore, it is very unlikely that trapping of magnesium atoms in cryogenic solid hydrogen will be worth the effort.

Aluminum seems to be an intermediate case in terms of I_{sp} increase. The gains in specific impulse are greater than lithium and magnesium, but less than boron and carbon. The potential gain (Fig. 8b) is very similar to nitrogen, except that aluminum always needs oxygen to give an optimum I_{sp} (Fig. 8a). At the 7% level, aluminum in solid hydrogen results in about 50 seconds increase in specific impulse and requires about 5% liquid oxygen.

EXHAUST PRODUCT CONTOUR CALCULATIONS

The Theoretical I_{sp} Program (5) also has the capability to tabulate output products in the chamber, throat, and exhaust. Contour plots of the exhaust products can show the reasons for the changes in the specific impulse curves. Essentially these plots detail the variations in the chemical composition of the exhaust products, which is also related to the exhaust temperature and the specific impulse. Figures 9 through 16 are chemistry contour plots for the above listed atoms in solid hydrogen.

In each figure, the first contour plot (always labeled "a") shows the overall trend for each exhaust product. These plots show the global picture for each atomic or molecular product and how these products relate to each other in terms of the mole percentages of the additive and oxidizer. The exact shape and contour should not be taken too seriously since the minimum levels for each specie differ. These "global" plots are provided to show only the general area of each exhaust product.

The data points for these plots are spaced at 1% intervals (as are the previous I_{sp} contour plots) and plotted using a program capable of 3D contour maps that interpolate between points and smooths rough edges. The interaction between the program and the data can result in variations in the contours that are dependent upon the input parameters to the plotting program. When interpreting these plots, consider this caveat.

For each additive, the output product contours are plotted separately to show the variations in concentration in greater detail. The contour numbers are derived from the output of the I_{sp} program, which gives product species concentrations in moles (of product species) per 100 grams of exhaust. The phase of the product is specifically labeled when the product is a solid or liquid. Exhaust products that do not have a phase label are always gaseous.

Hydrogen Atoms

The output products for combustion of hydrogen atoms in solid hydrogen are mainly liquid water and steam, essentially the same as for liquid hydrogen / LOX combustion. At higher LOX and hydrogen atom concentrations, both H atoms and OH radicals increase, indicating losses from incomplete recombination. This same area in the specific impulse contour plot shows greatly reduced performance values, as expected. At low hydrogen atom and LOX concentrations, liquid water is produced in the exhaust stream as a result of relatively low exhaust temperatures. This is also a region of low specific impulse values.

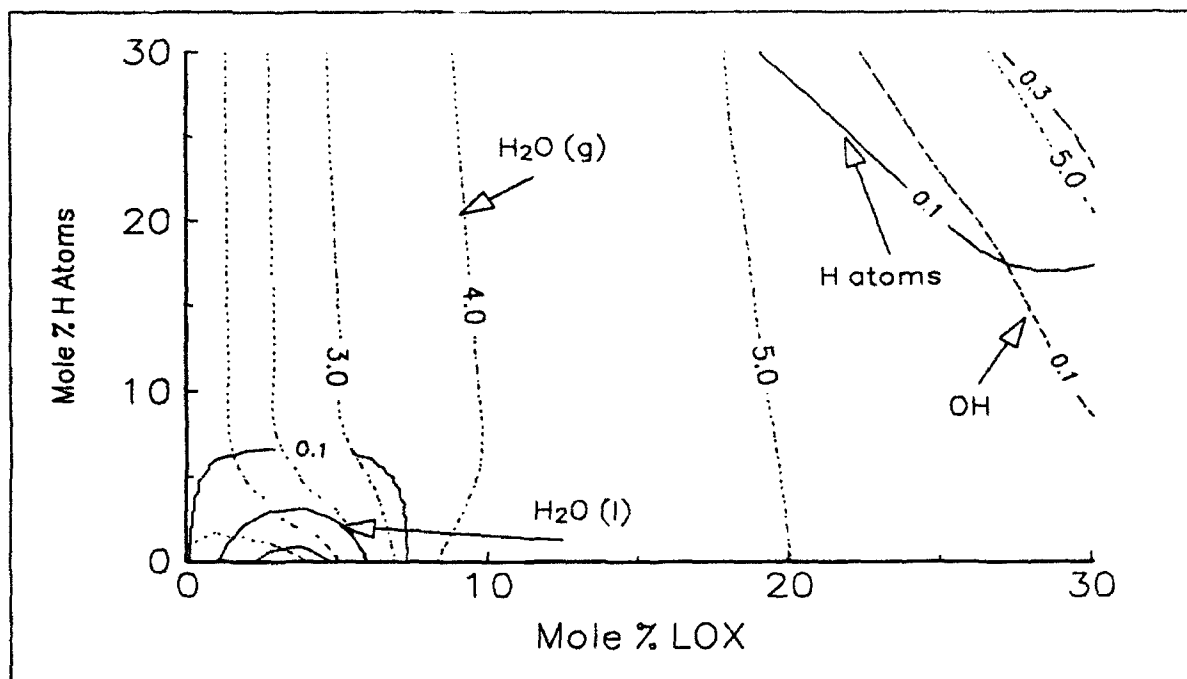


FIGURE 9a
Exhaust Product Contour Plot for Hydrogen

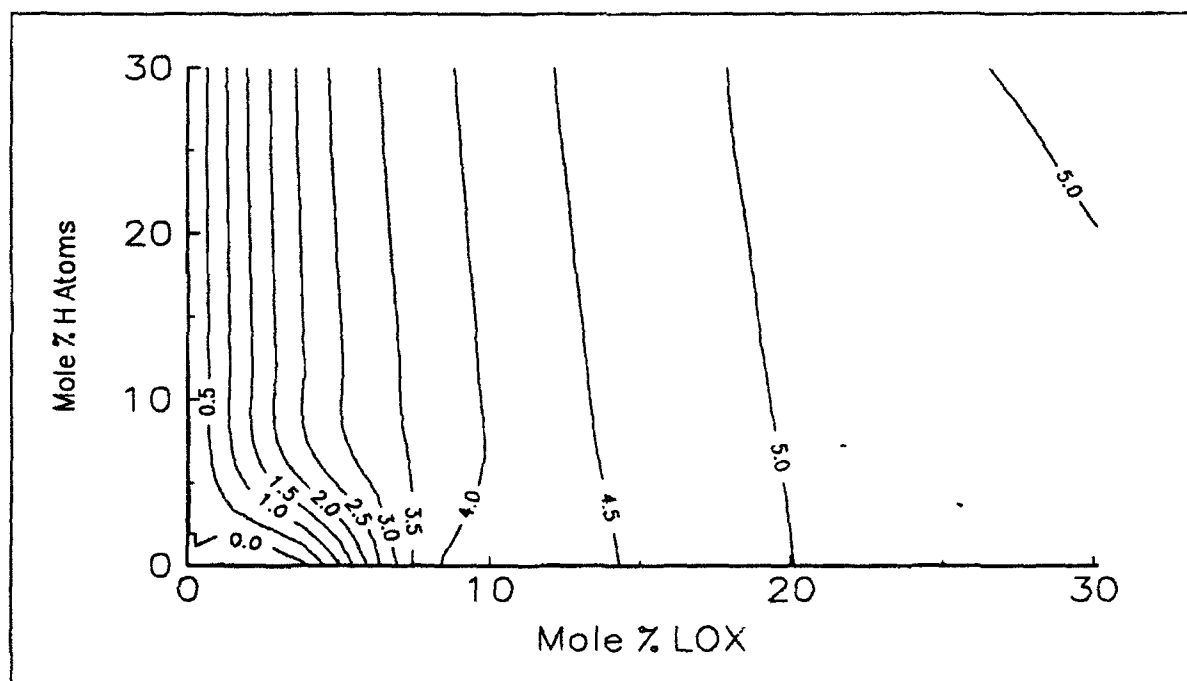


FIGURE 9b
Exhaust Product Contour Plot for H₂O

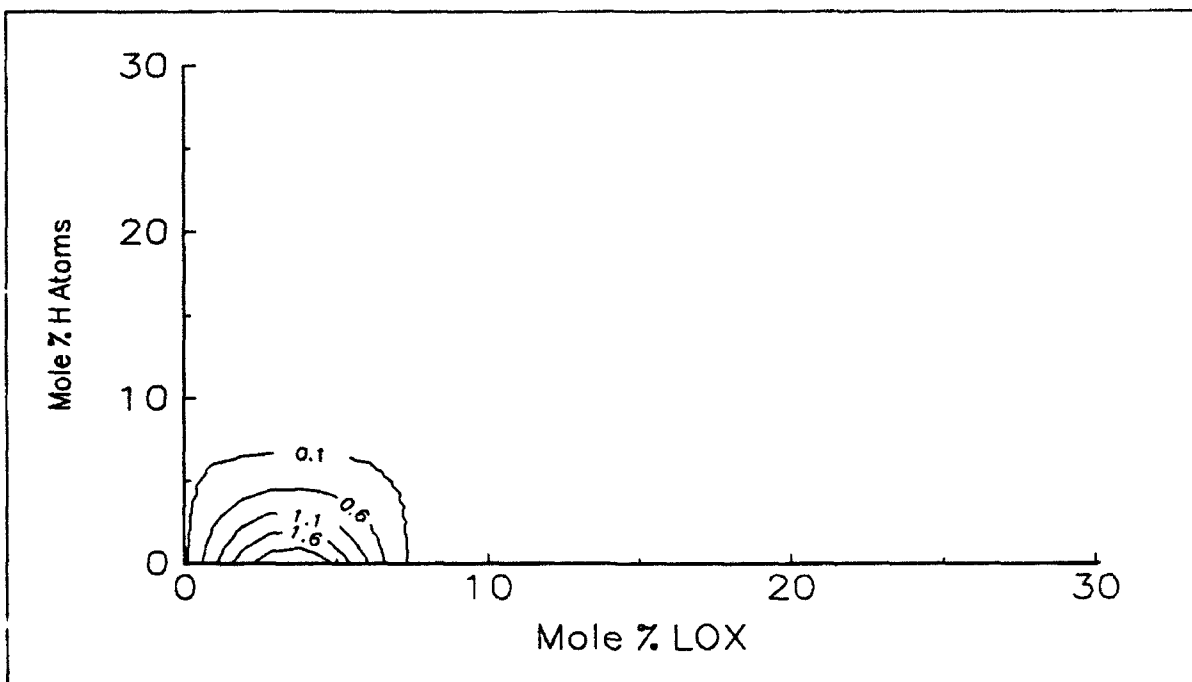


FIGURE 9c
Exhaust Product Contour Plot for H₂O (liquid)

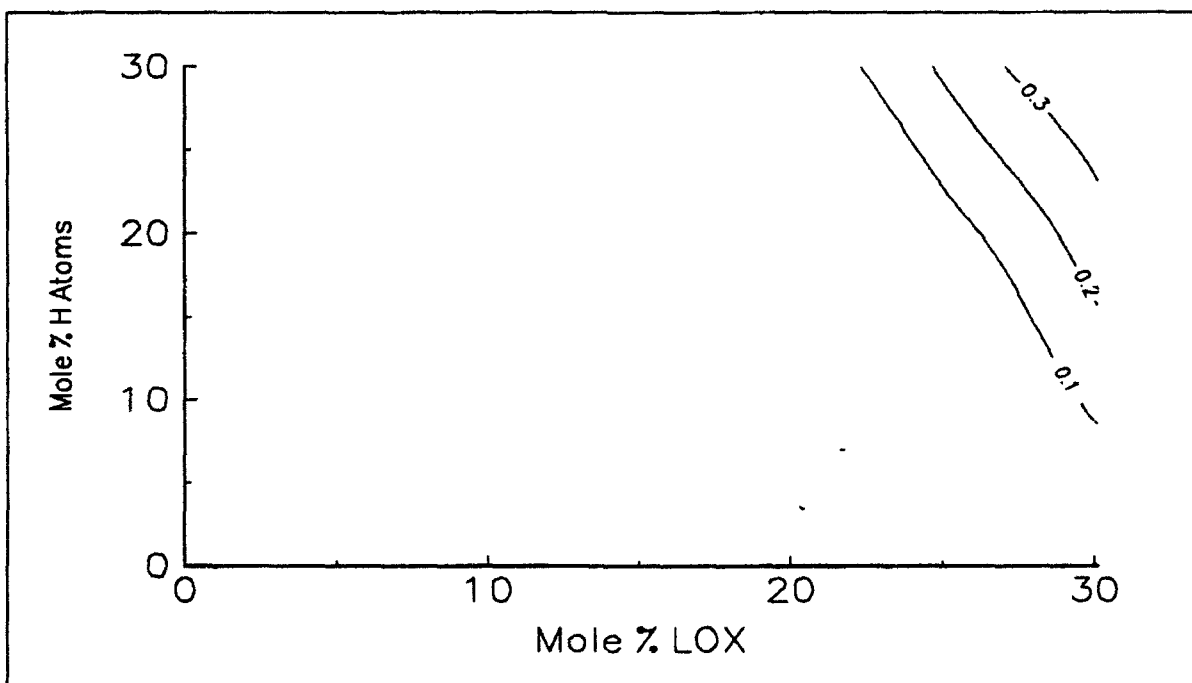


FIGURE 9d
Exhaust Product Contour Plot for OH

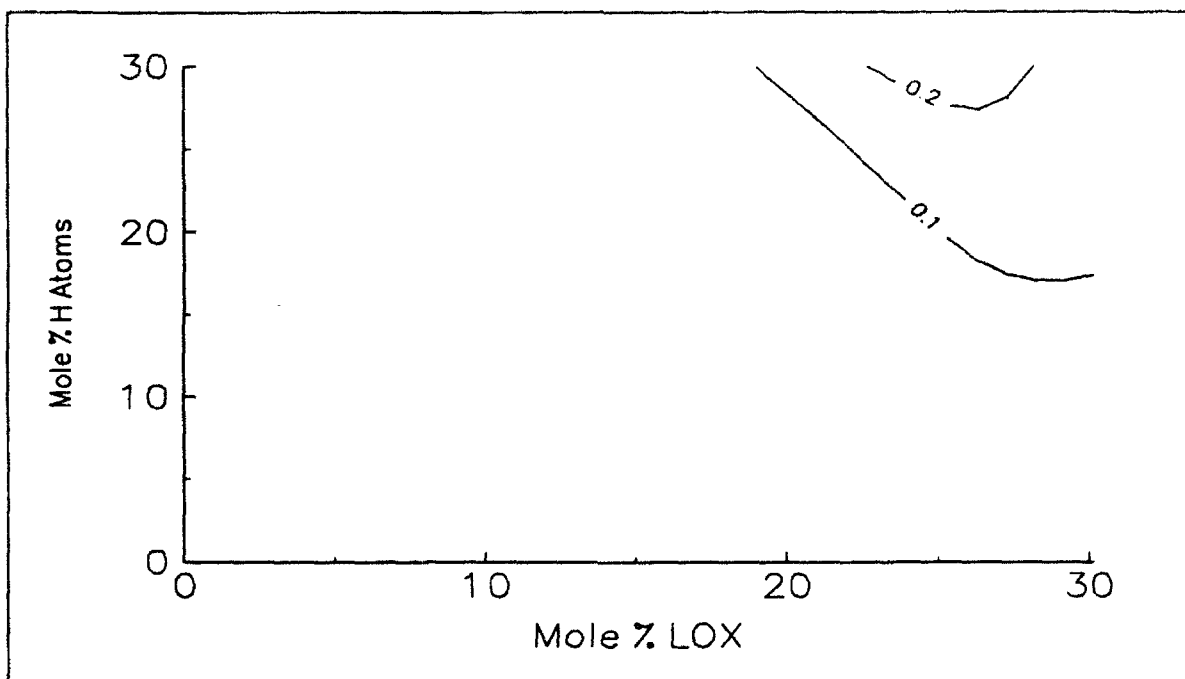


FIGURE 9e
Exhaust Product Contour Plot for H Atoms

Lithium Atoms

The exhaust product contours for lithium atoms in solid hydrogen are considerably more complicated than the hydrogen contours. There are nine different major products and several minor products (not shown). The increase in unreacted lithium atoms (Fig. 10b) above 20 mole percent results in the limit of the specific impulse optimum to around that same value. The unreacted atoms result from an increase in the combustion temperature that drives the thermochemistry away from combustion with oxygen. At low oxygen concentrations, the major output products are liquid and solid LiH. The expected optimum product, Li_2O , occurs at fairly low oxygen levels. The solid phase of Li_2O corresponds to the optimum specific impulse region (see Fig. 2a). The partially lithiated output product, LiOH, is prevalent at higher oxidizer ratios or low lithium concentrations. As might be expected, this product is dominant when the lithium and LOX mole ratios are roughly equivalent, while the fully lithiated product, Li_2O , is prevalent when the lithium concentration is greater than the LOX concentration.

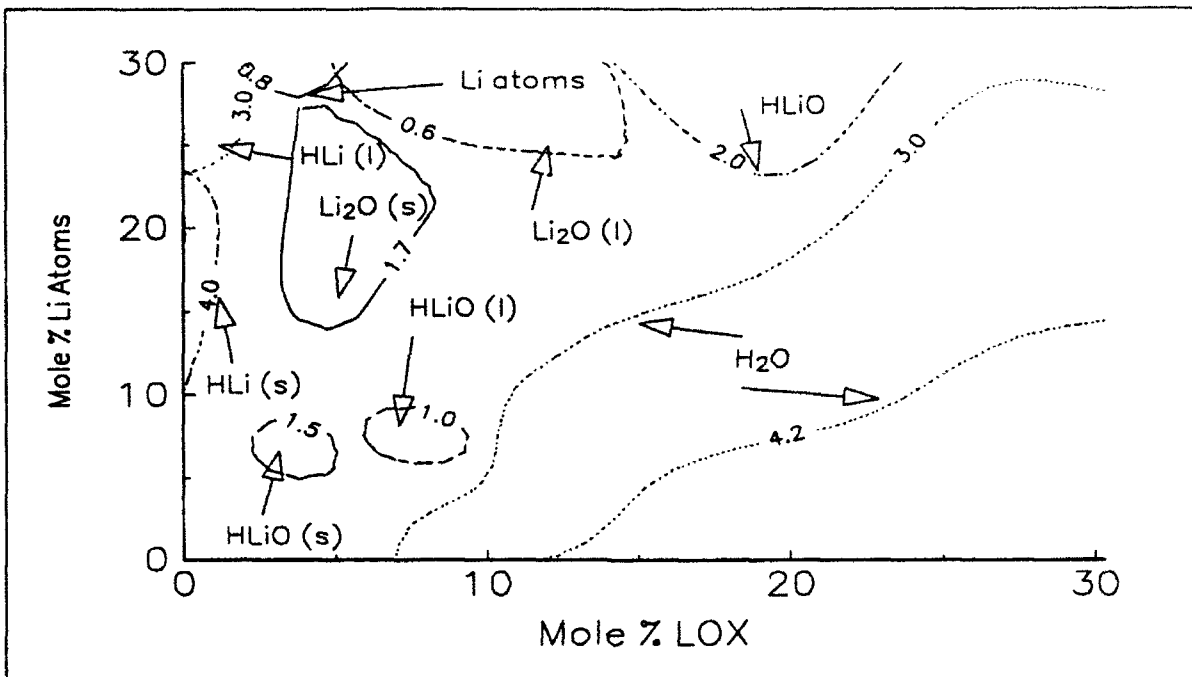


FIGURE 10a
Exhaust Product Contour Plot for Lithium

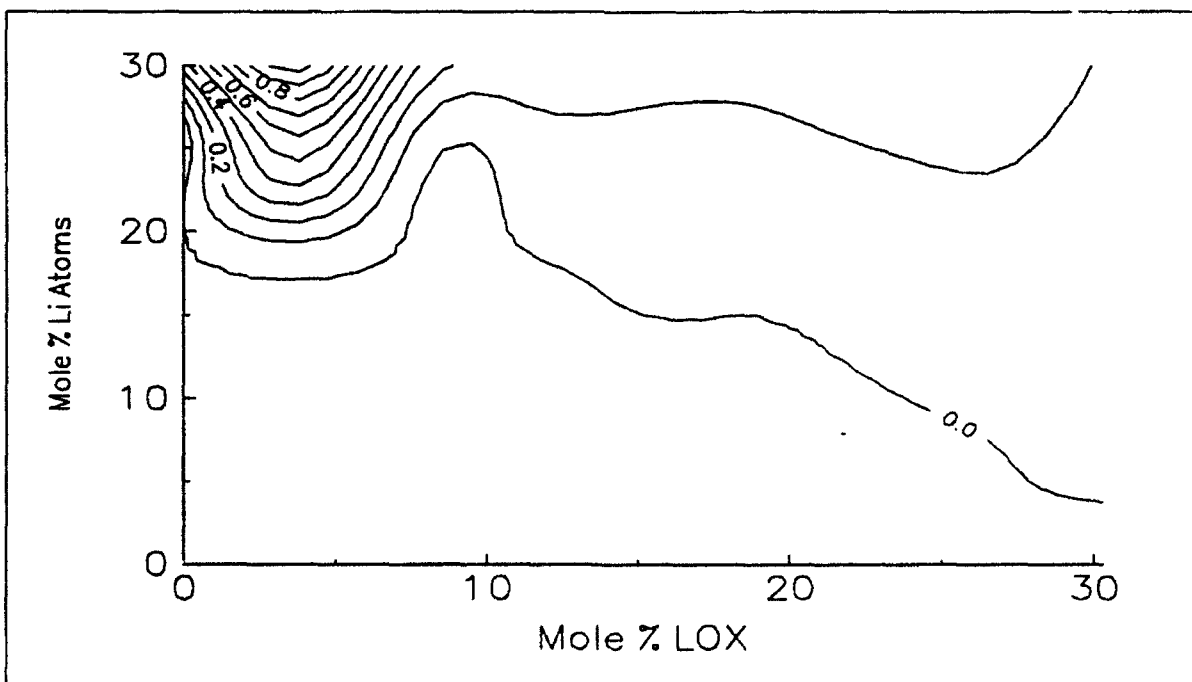


FIGURE 10b
Exhaust Product Contour Plot for Li Atoms

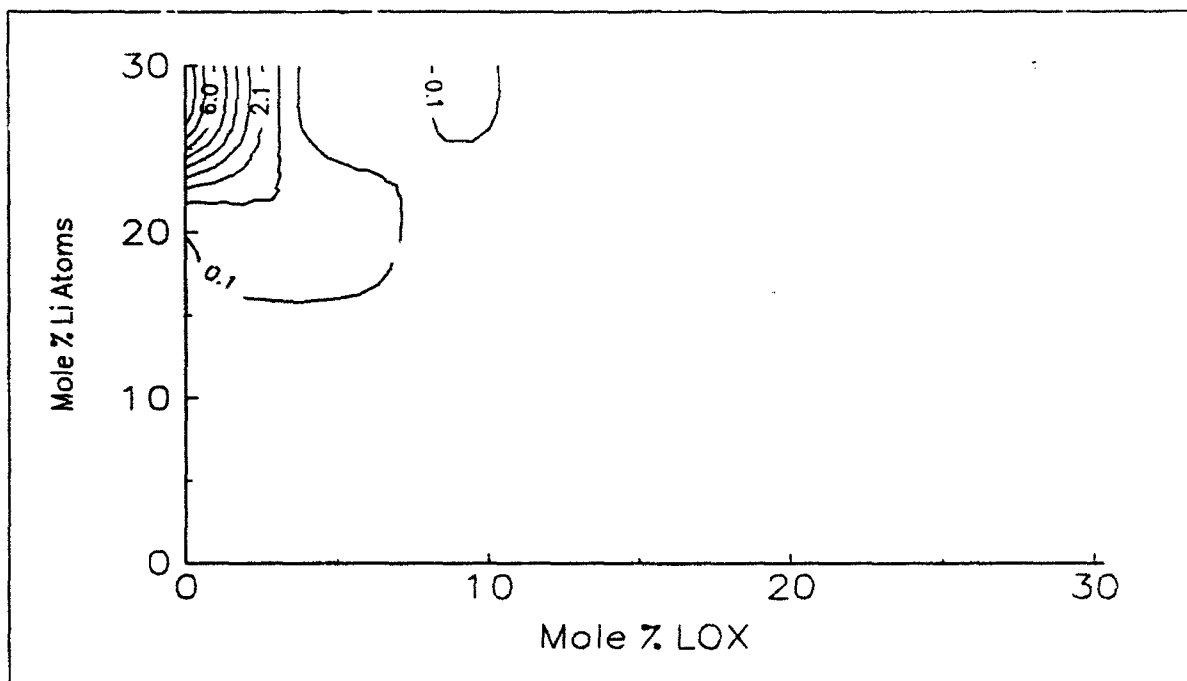


FIGURE 10c
Exhaust Product Contour Plot for LiH (liquid)

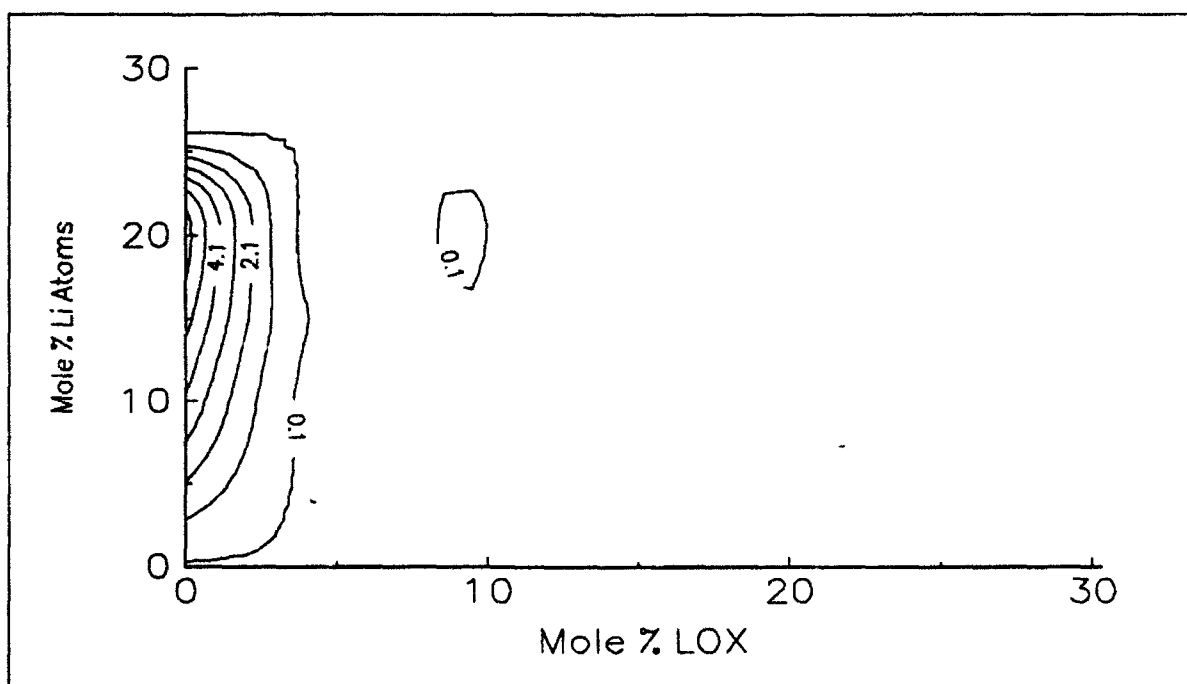


FIGURE 10d
Exhaust Product Contour Plot for LiH (solid)

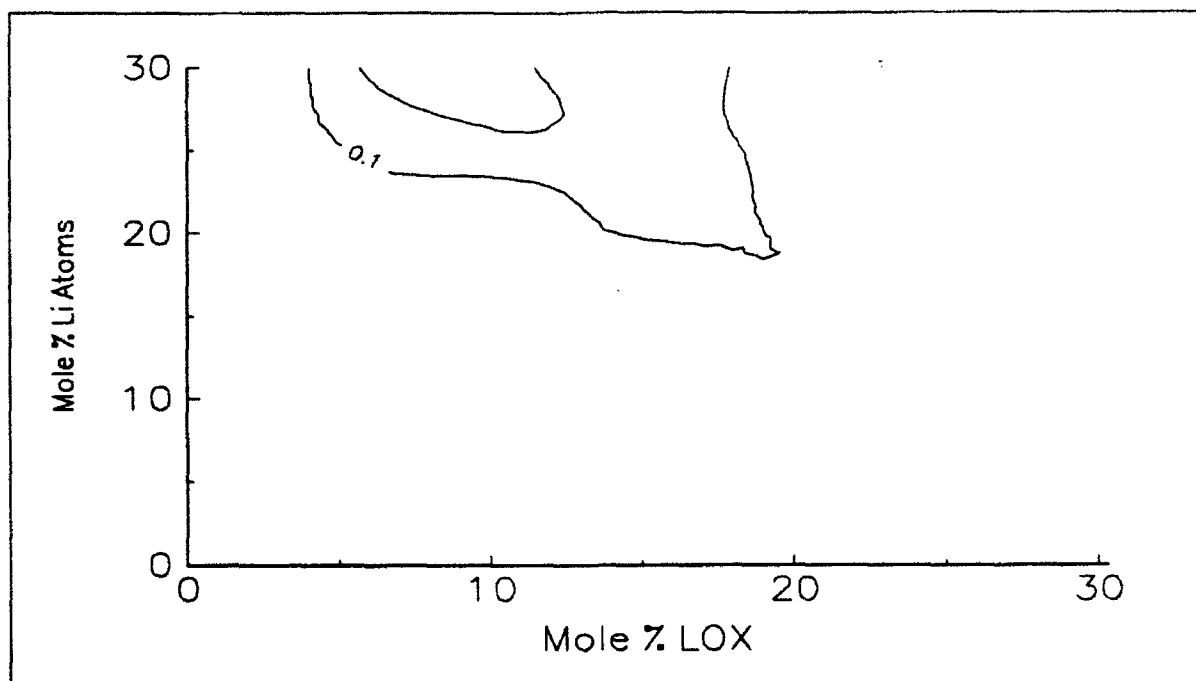


FIGURE 10e
Exhaust Product Contour Plot for Li_2O (liquid)

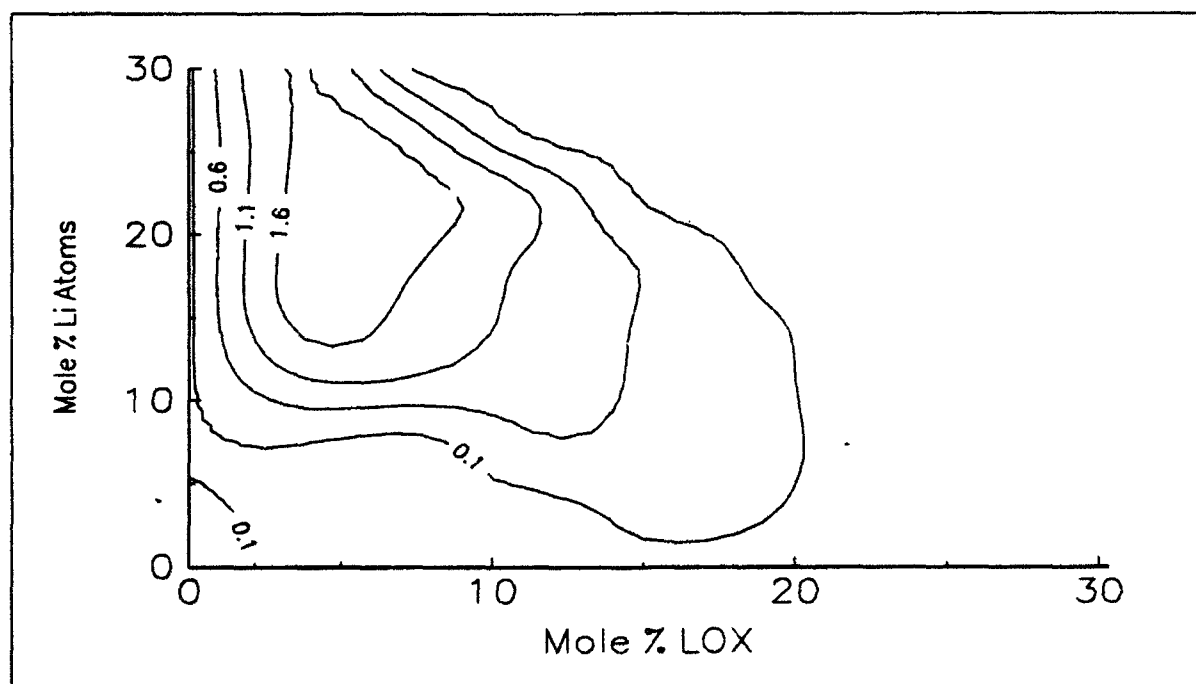


FIGURE 10f
Exhaust Product Contour Plot for Li_2O (solid)

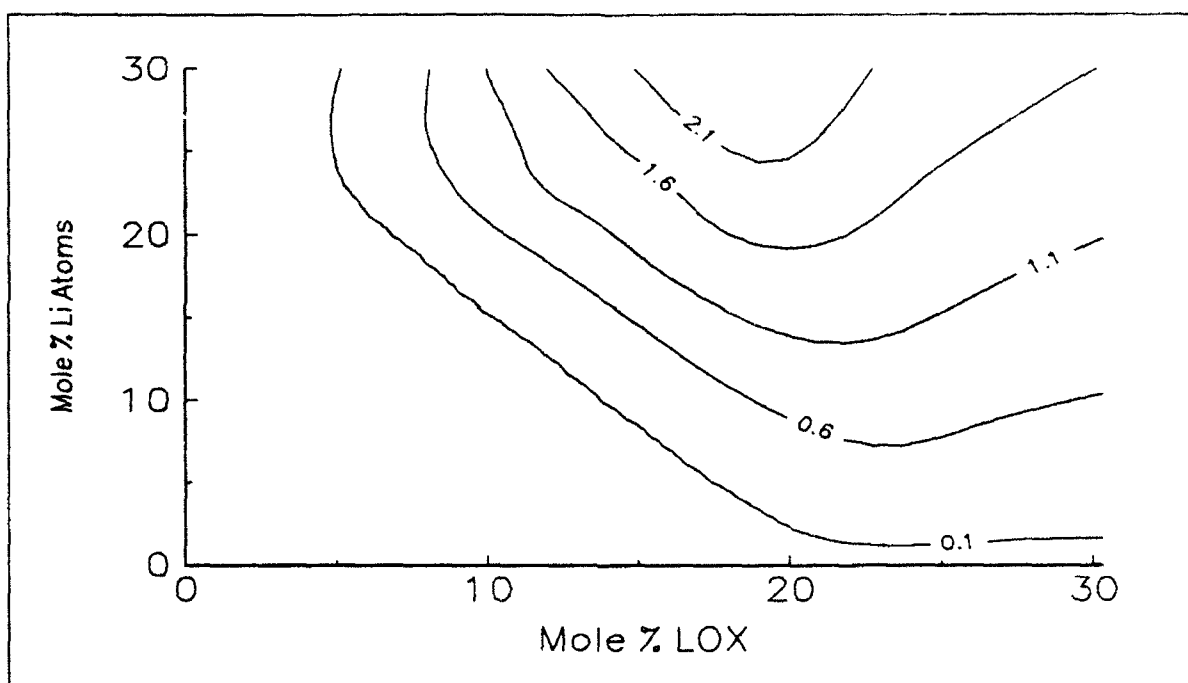


FIGURE 10g
Exhaust Product Contour Plot for HLiO

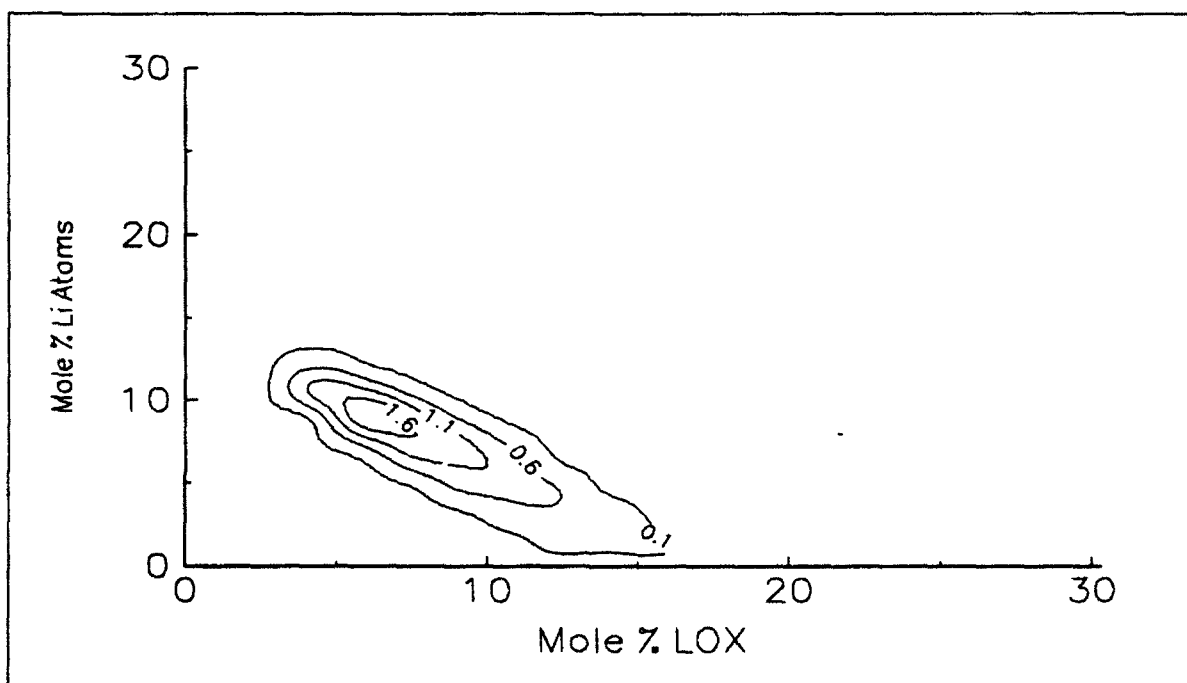


FIGURE 10h
Exhaust Product Contour Plot for HLiO (liquid)

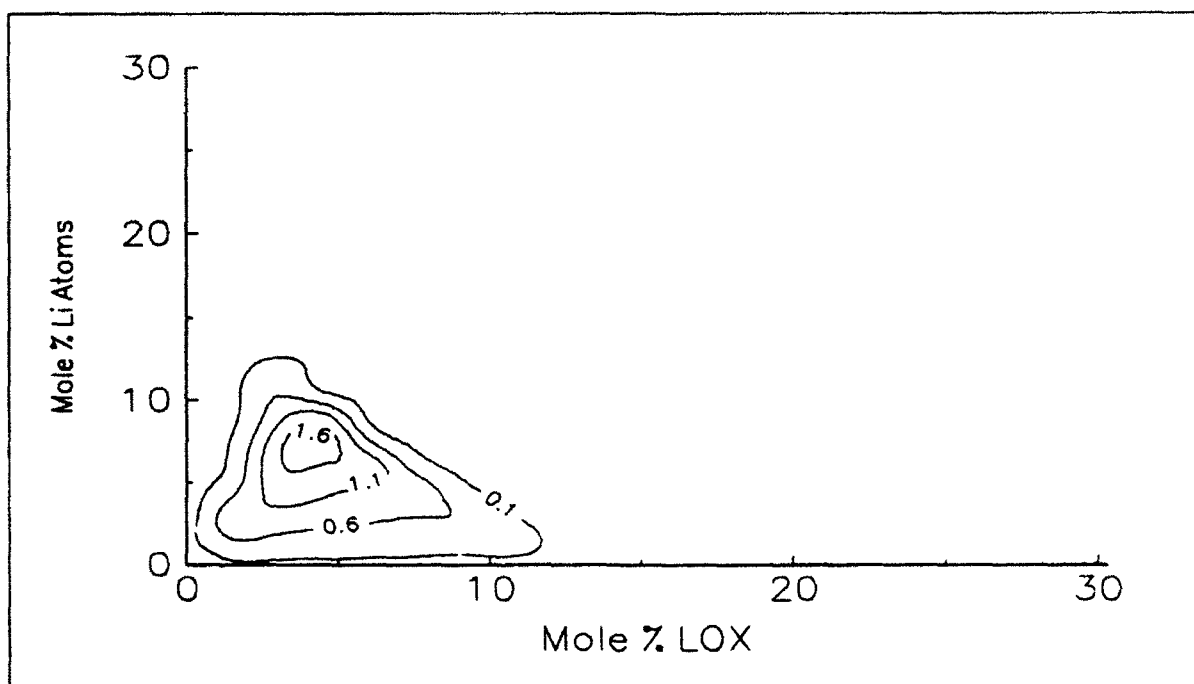


FIGURE 10i
Exhaust Product Contour Plot for HLiO (solid)

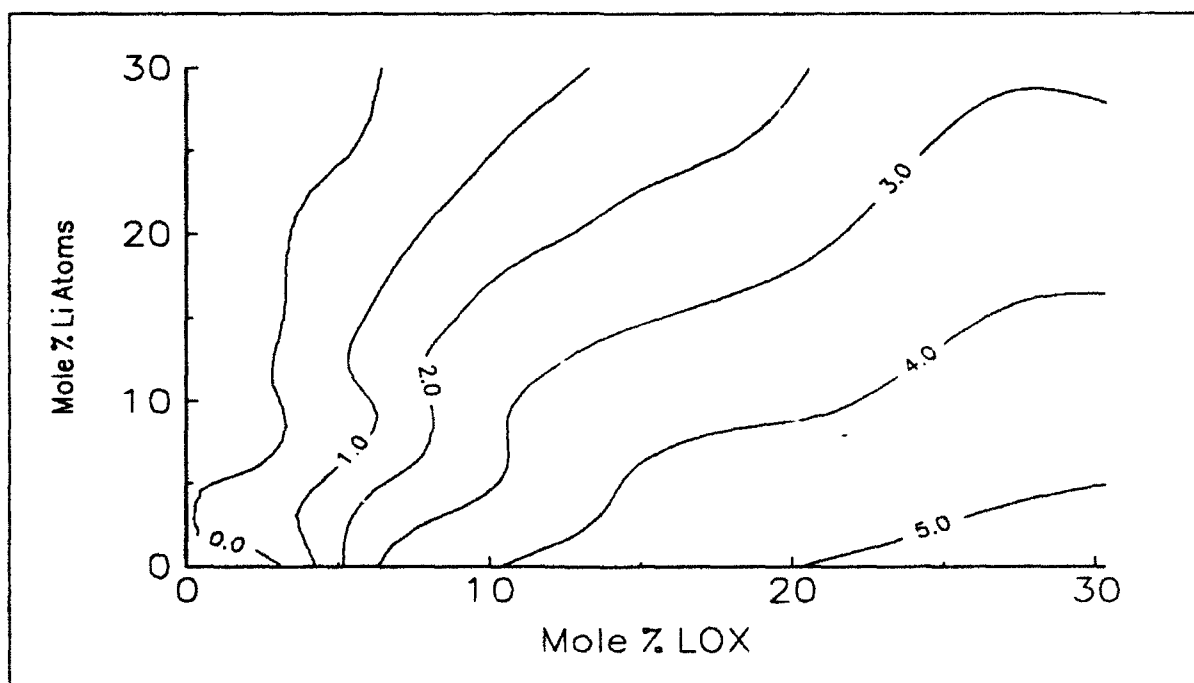


FIGURE 10j
Exhaust Product Contour Plot for H₂O

Beryllium Atoms

The contours for beryllium atoms contain eight major output products. At low oxidizer levels, uncombusted beryllium is prevalent in solid form at relatively low atom concentrations and as a liquid or gas at higher concentrations. As with lithium, the optimum product, BeO, is prevalent when the atom and LOX concentrations are relatively equal. The solid alpha phase of BeO corresponds to the optimum specific impulse region, as can be seen from a comparison of Figures 3a and 11e. At high LOX concentrations, the major Be containing species begins to shift to beryllium hydroxide (BeH_2O_2). Once again, please note that the waviness of the contours, especially at low levels, is mostly an effect of the plotting program and should be considered to contain some degree of error.

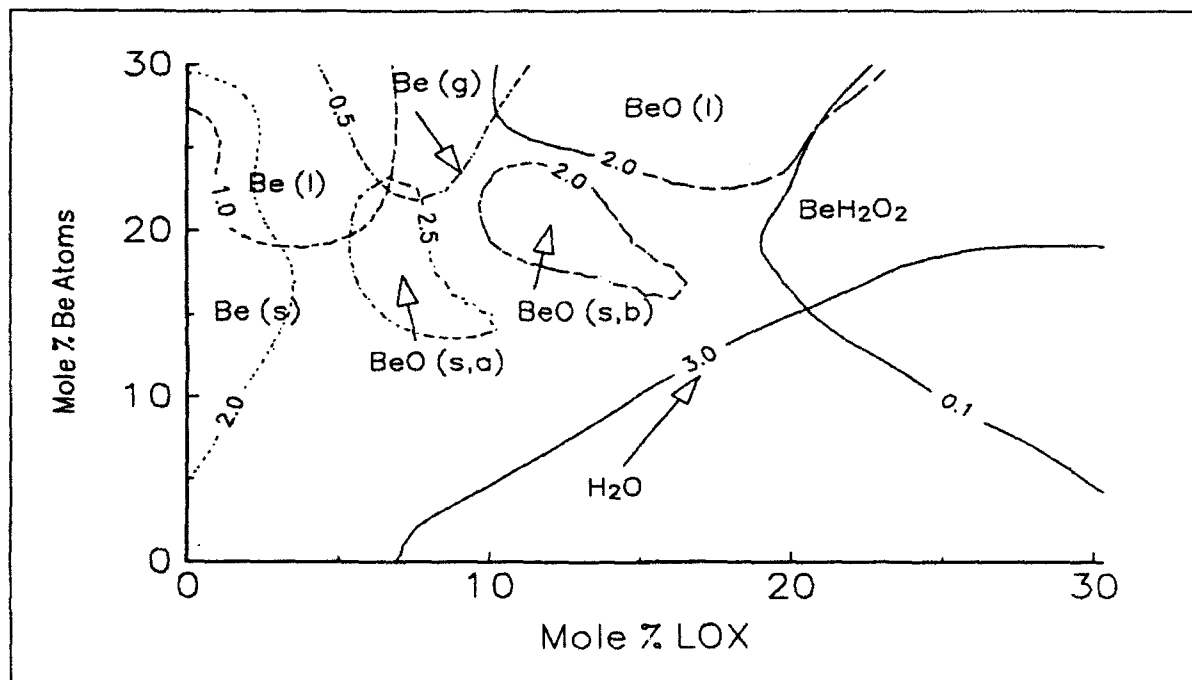


FIGURE 11a
Exhaust Product Contour Plot for Beryllium

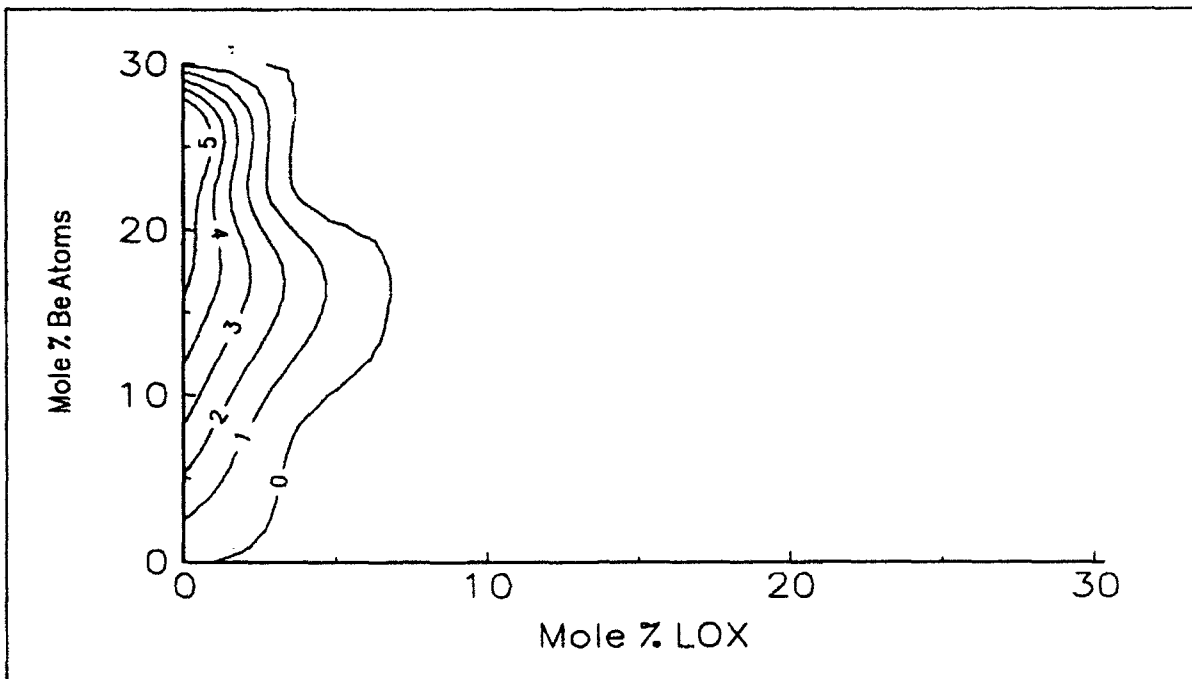


FIGURE 11b
Exhaust Product Contour Plot for Be (s)

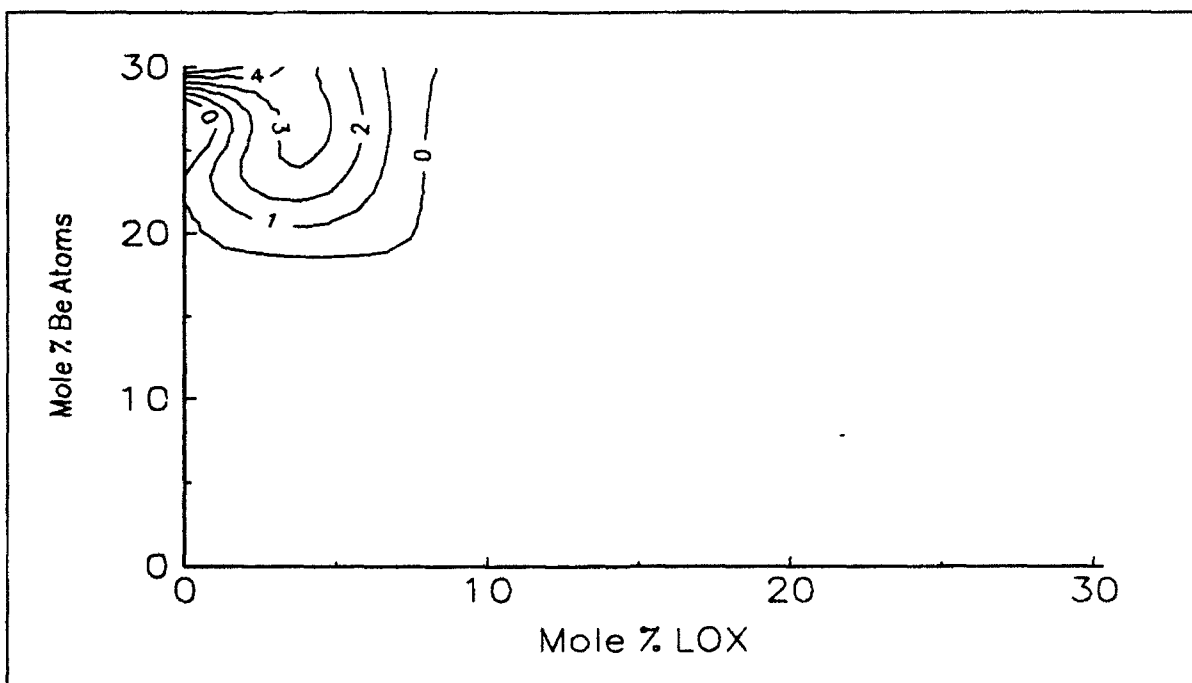


FIGURE 11c
Exhaust Product Contour Plot for Be (l)

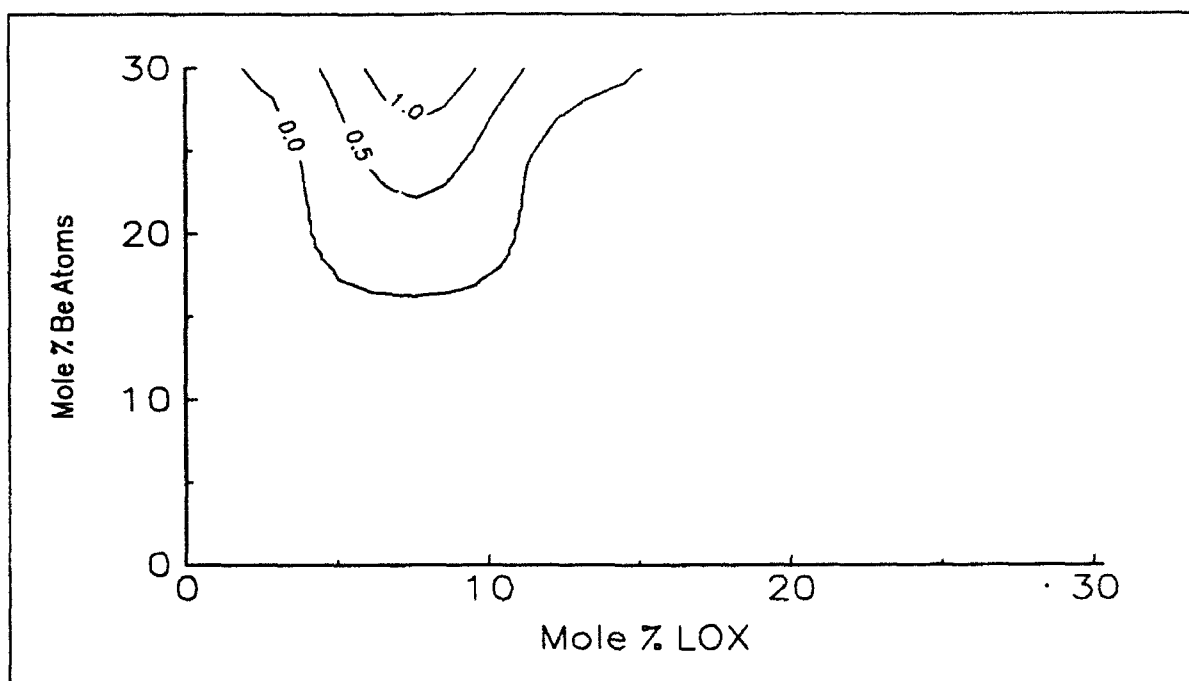


FIGURE 11d
Exhaust Product Contour Plot for Be (g)

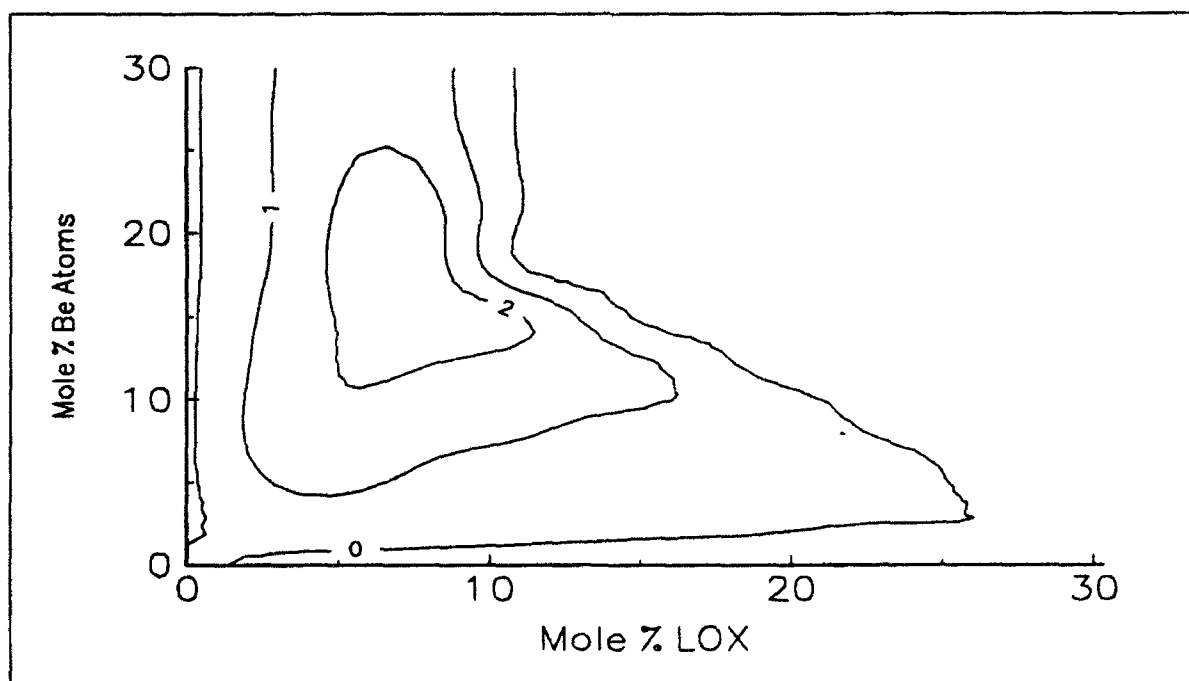


FIGURE 11e
Exhaust Product Contour Plot for BeO (s,a)

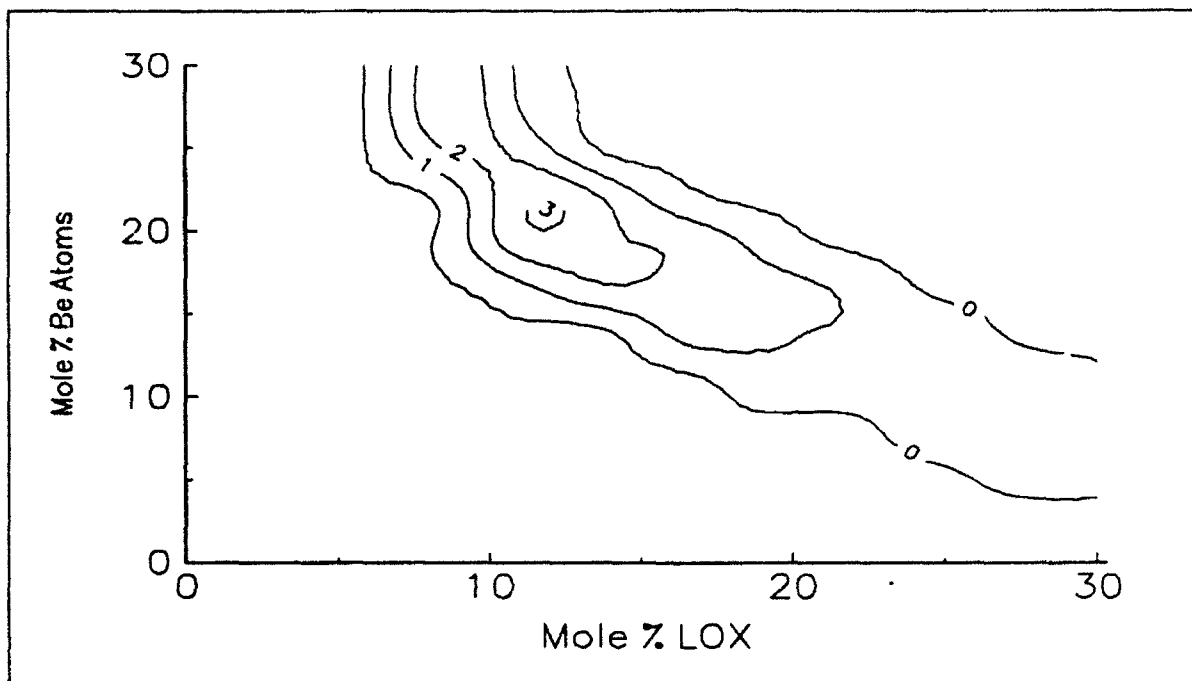


FIGURE 11f
Exhaust Product Contour Plot for BeO (s,b)

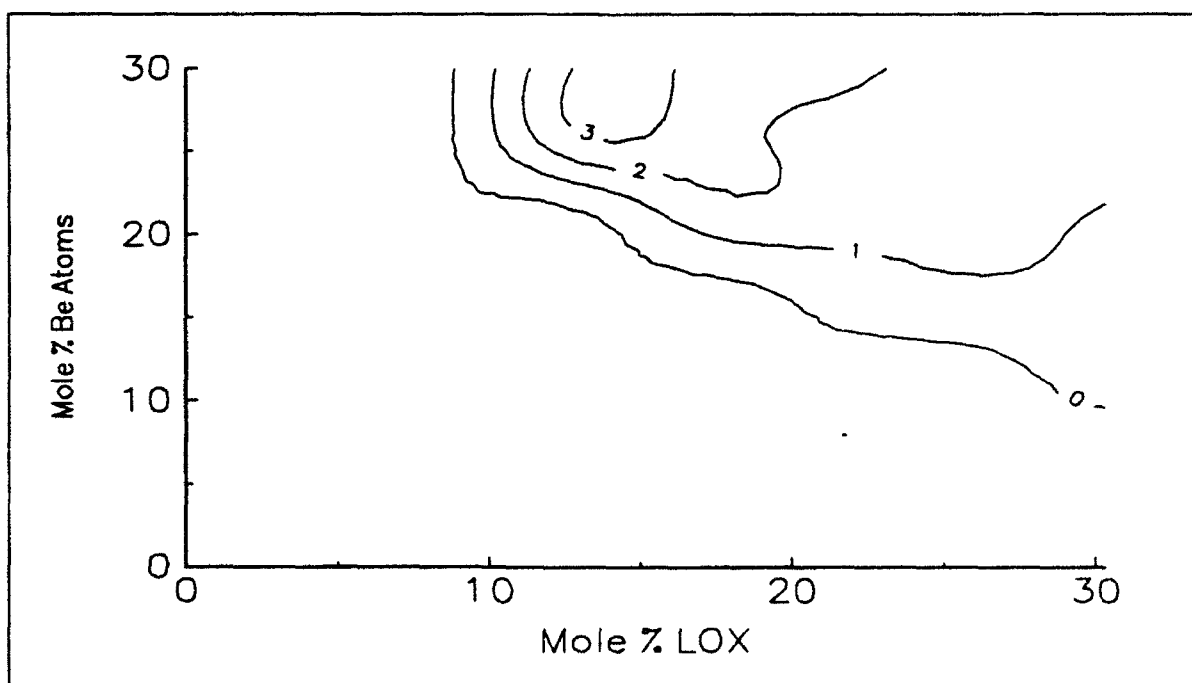


FIGURE 11g
Exhaust Product Contour Plot for BeO (l)

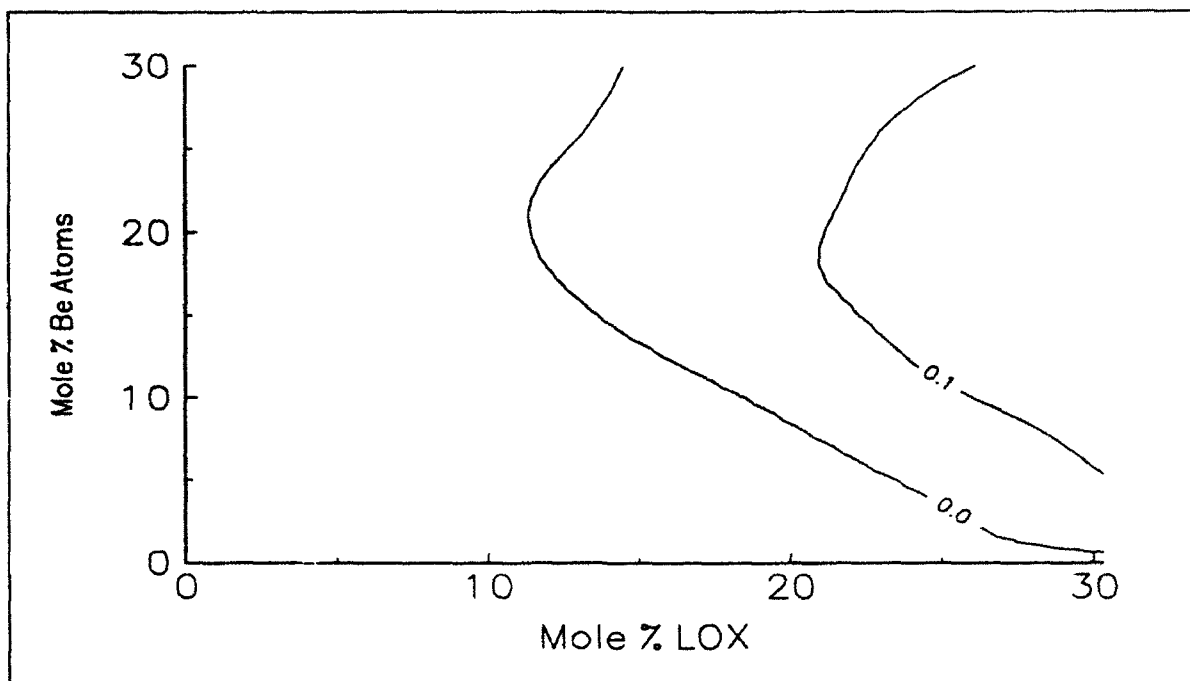


FIGURE 11h
Exhaust Product Contour Plot for BeH₂O₂

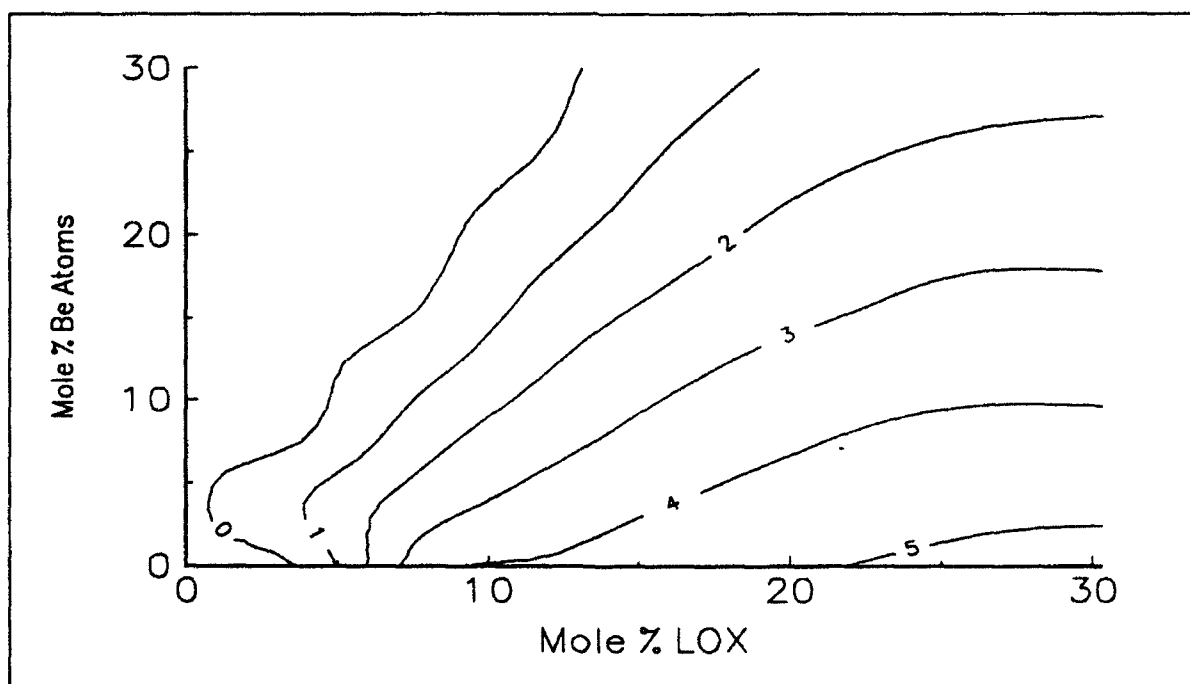


FIGURE 11i
Exhaust Product Contour Plot for H₂O

Boron

There are nine major exhaust products for combustion of boron atoms in solid hydrogen with liquid oxygen. Solid boron is formed at high boron atom concentrations and low LOX amounts. This same region also corresponds to the maximum specific impulse region. Both BO and HBO are also formed at high boron atom concentrations, depending on the oxidizer concentrations. At moderate boron atom levels, both HOBO and B_2O_3 are prevalent. There is a shift from HOBO to B_2O_3 when the liquid oxygen level is reduced from $LOX > B$ atoms to $LOX < B$ atoms. The optimum specific impulse levels for potentially obtainable concentrations of boron atoms (i.e., 1 to 8 mole percent boron atoms with about 5 mole percent LOX) correspond mostly to the B_2O_3 regions. Perhaps the best system for boron would be 7 mole % boron atoms in solid hydrogen combusted with 5 mole % LOX, giving an I_{sp} increase of about 100 seconds (over LH_2 / LOX) and B_2O_3 (liquid) as the major exhaust product.

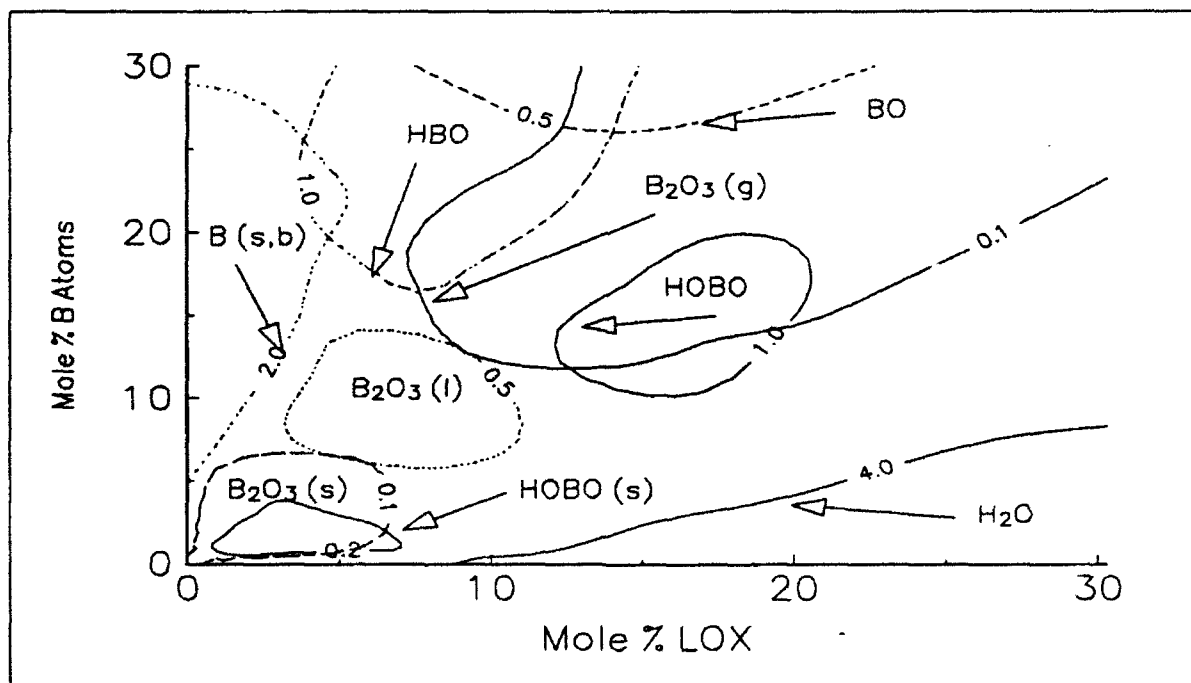


FIGURE 12a
Exhaust Product Contour Plot for Boron

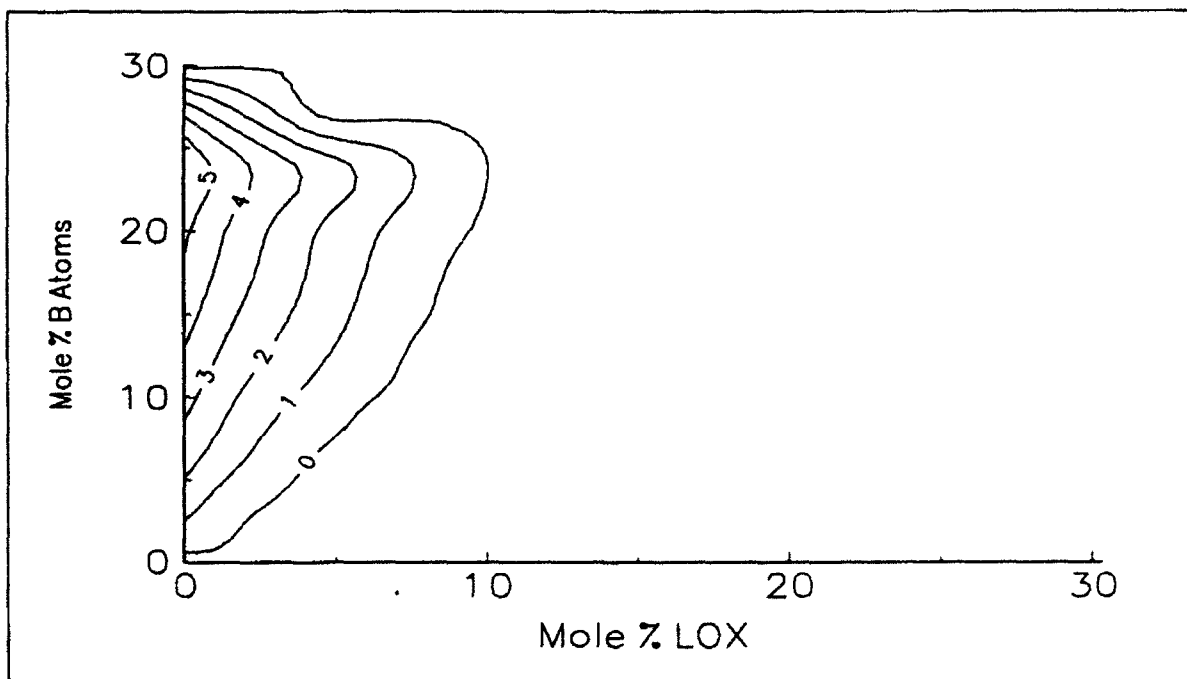


FIGURE 12b
Exhaust Product Contour Plot for B (s,b)

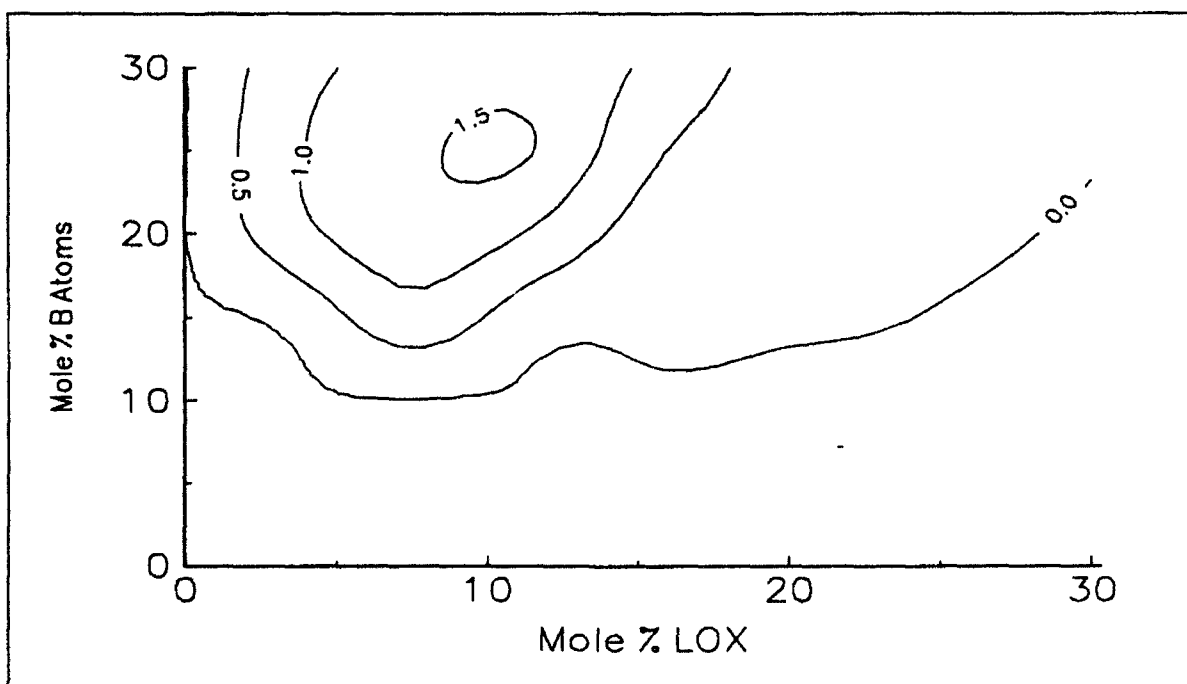


FIGURE 12c
Exhaust Product Contour Plot for HBO

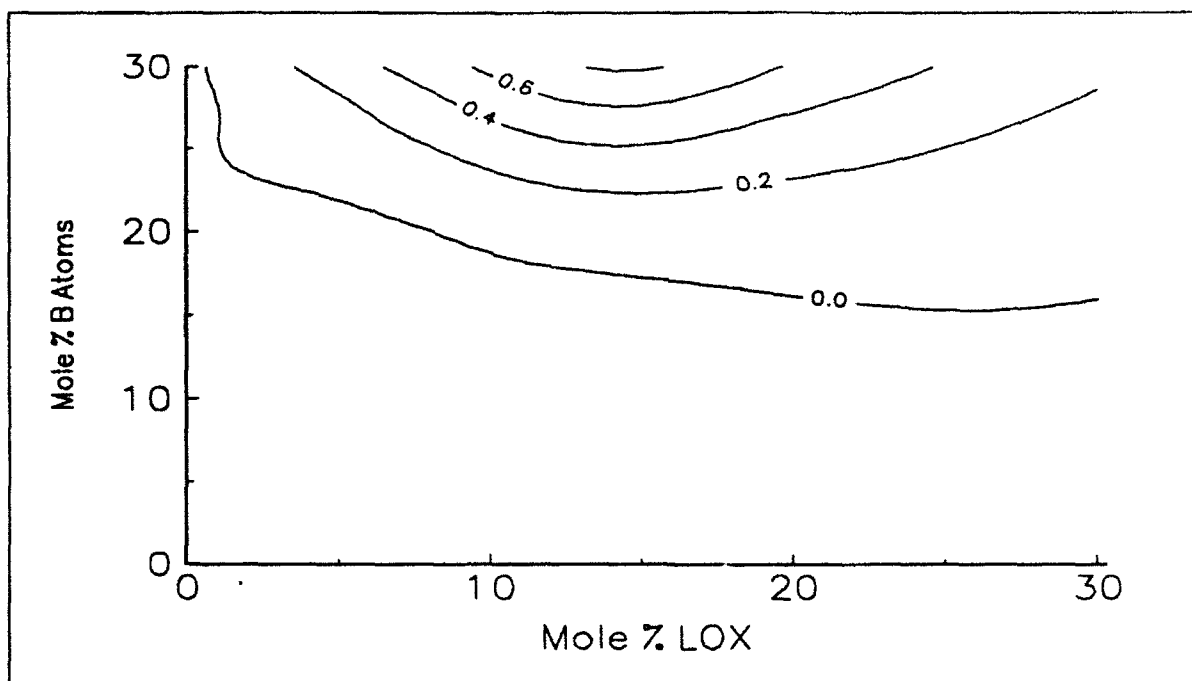


FIGURE 12d
Exhaust Product Contour Plot for BO

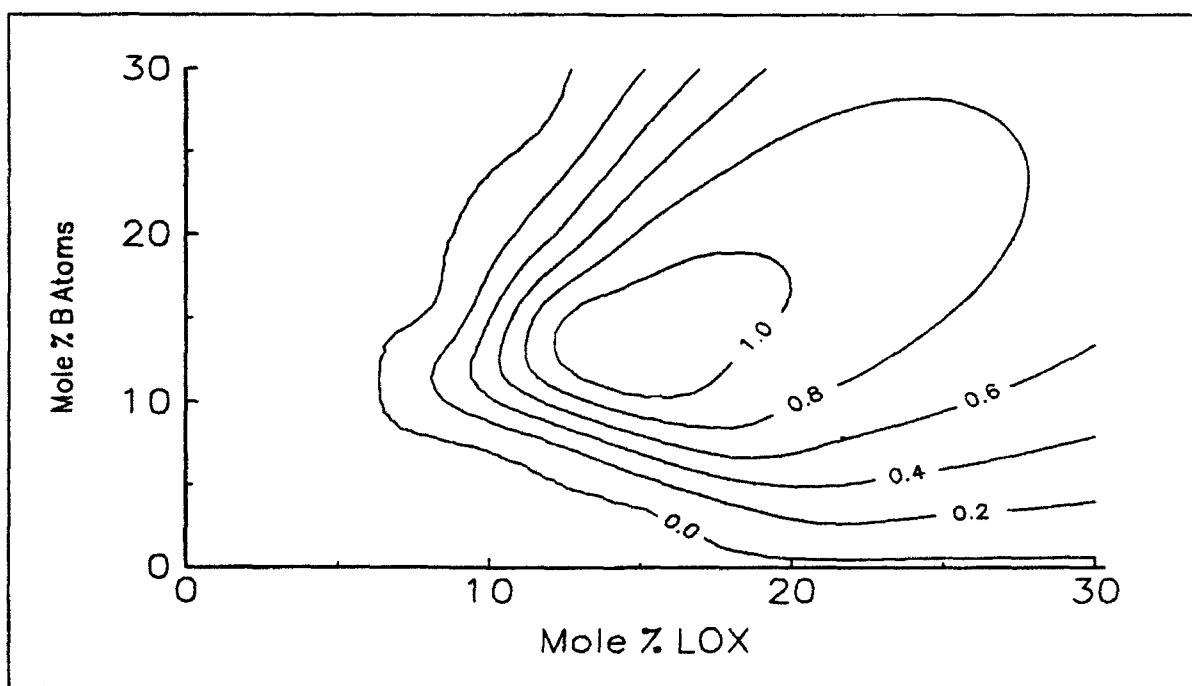


FIGURE 12e
Exhaust Product Contour Plot for HOBO

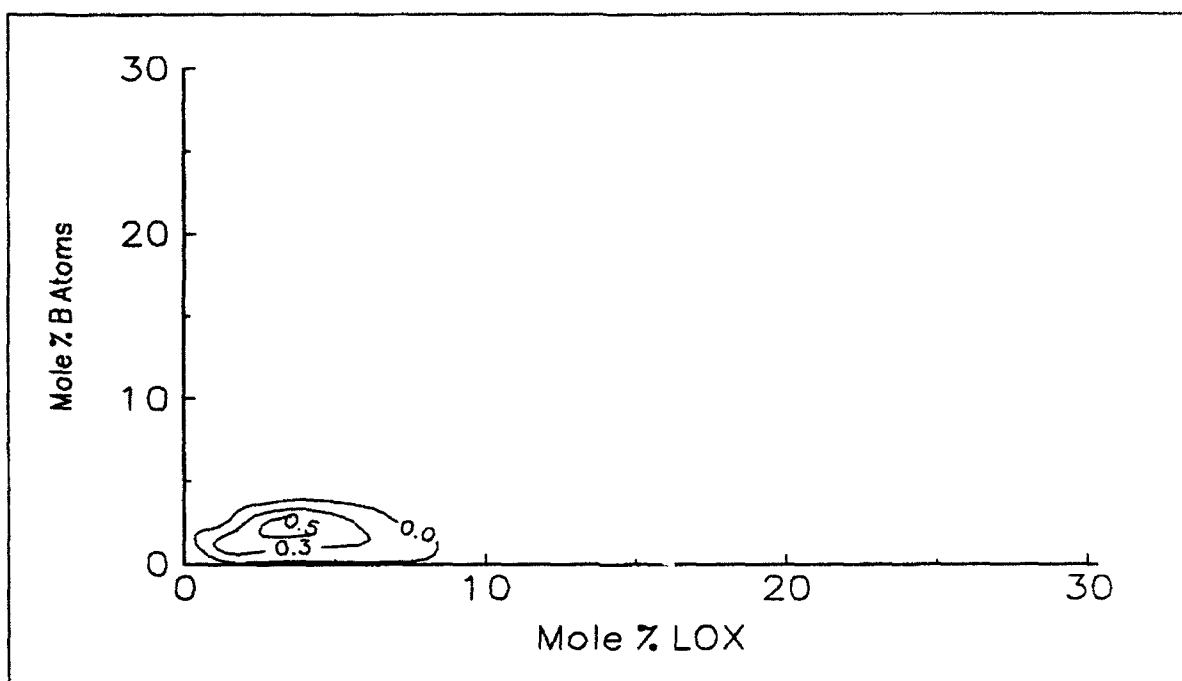


FIGURE 12f
Exhaust Product Contour Plot for HOBO (s)

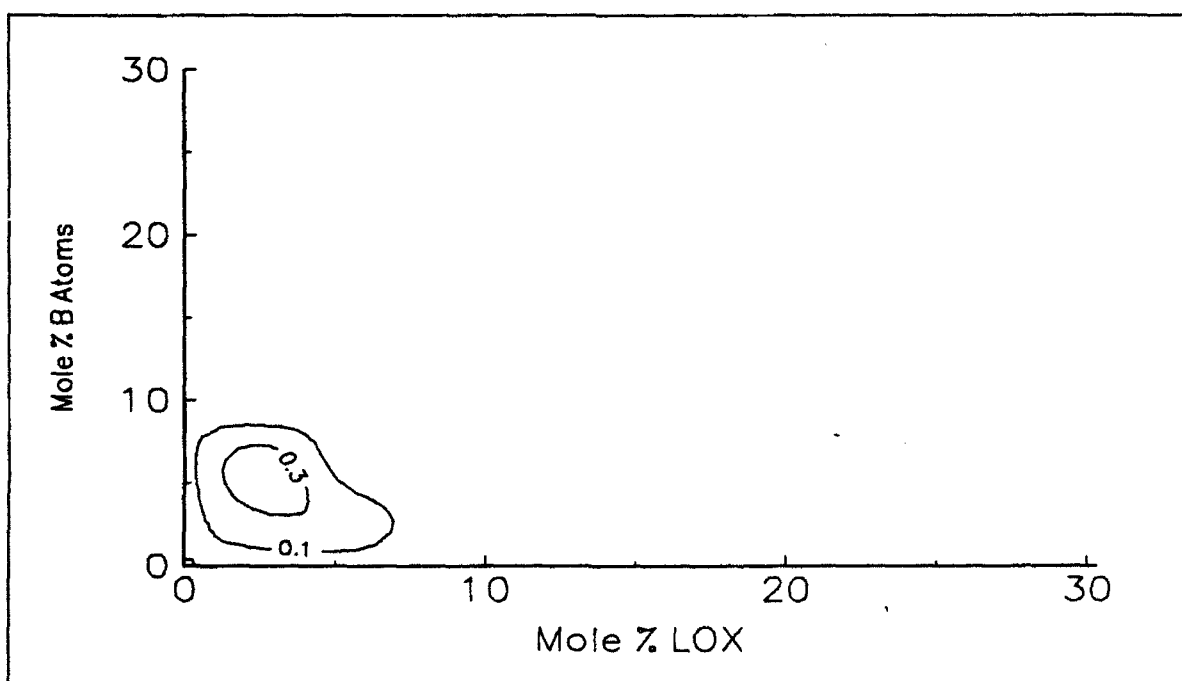


FIGURE 12g
Exhaust Product Contour Plot for B₂O₃ (s)

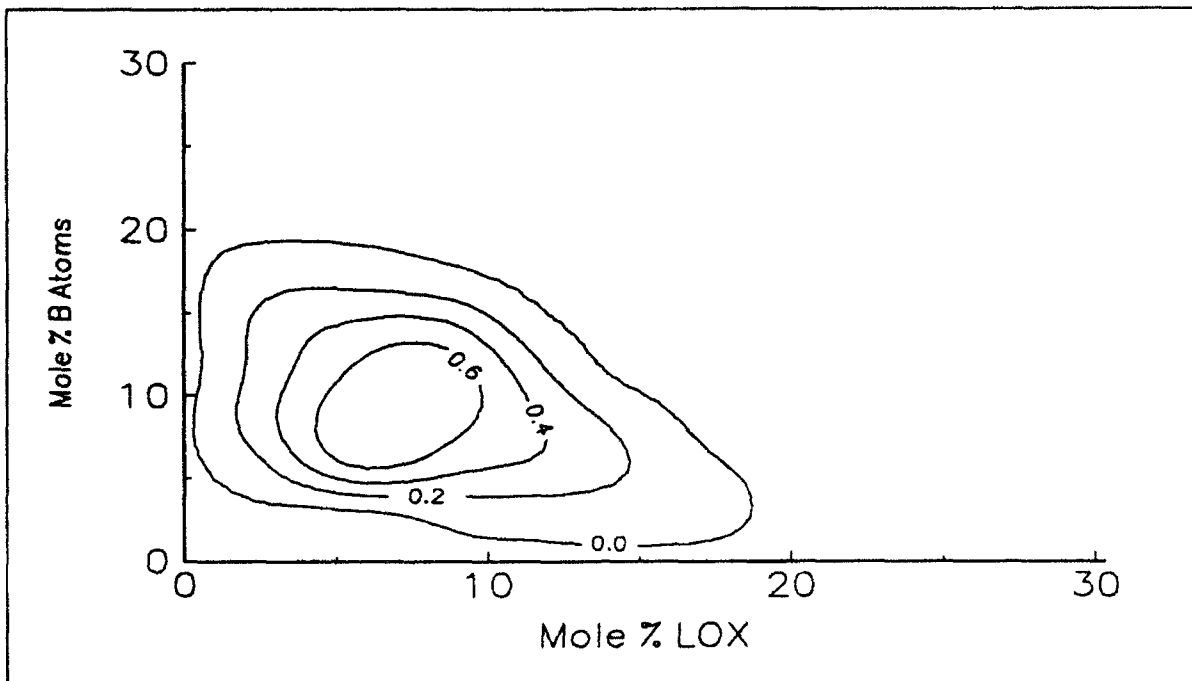


FIGURE 12h
Exhaust Product Contour Plot for B_2O_3 (l)

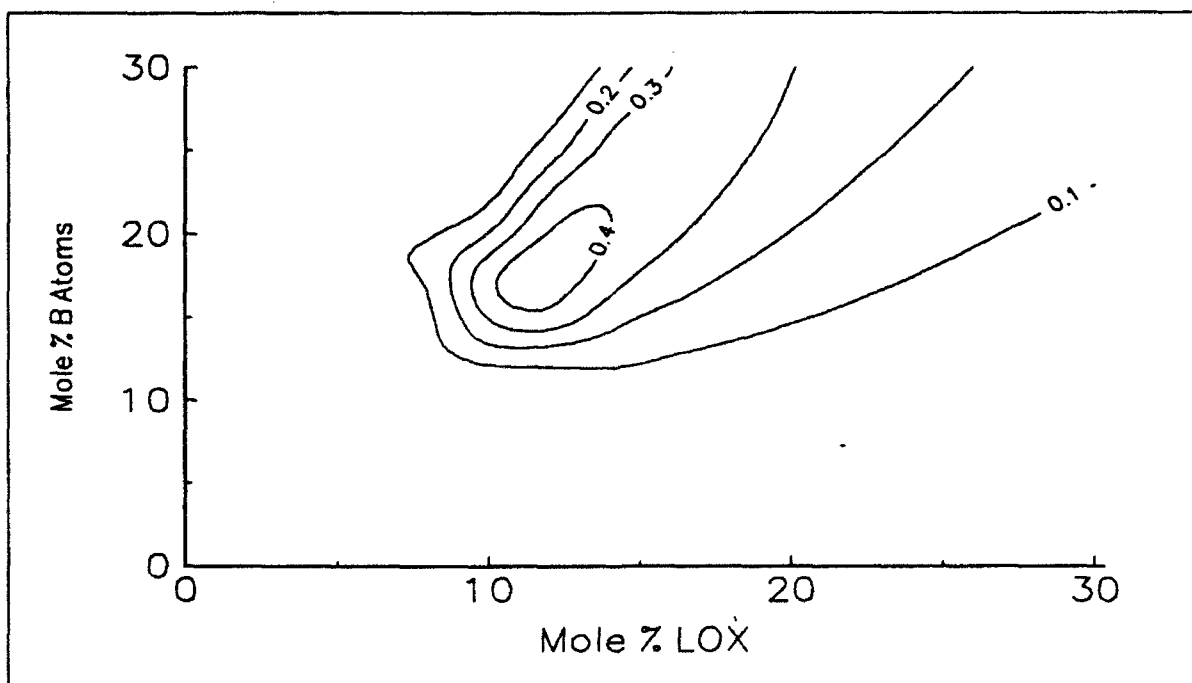


FIGURE 12i
Exhaust Product Contour Plot for B_2O_3 (g)

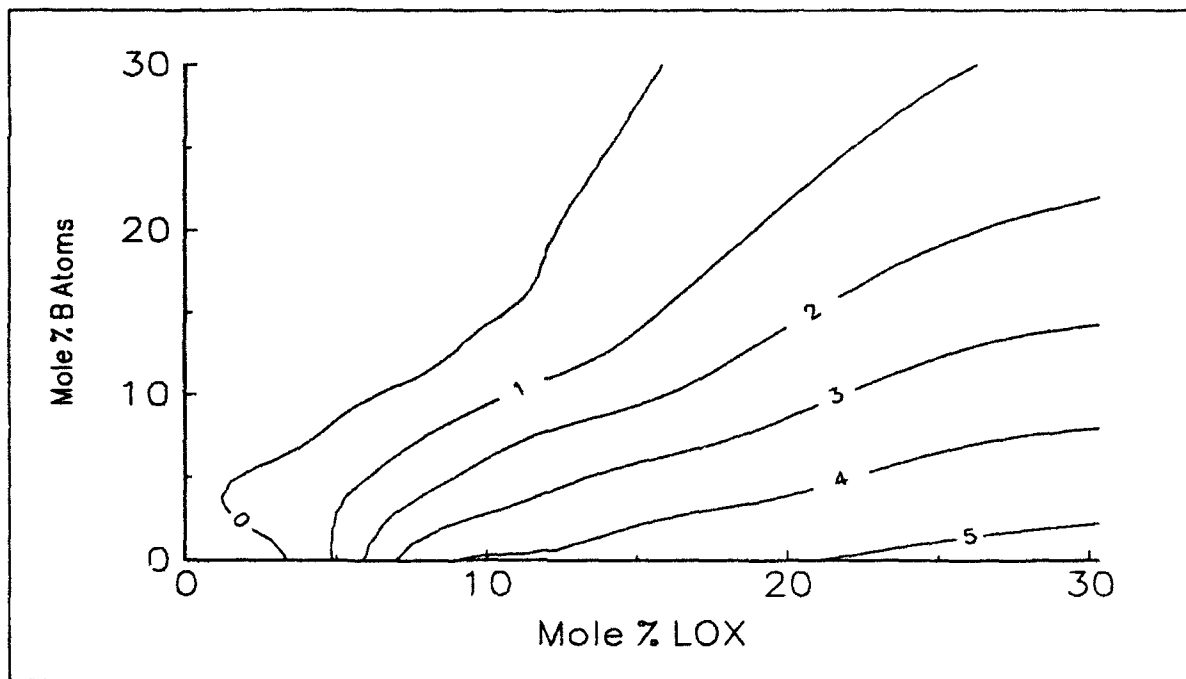


FIGURE 12j
Exhaust Product Contour Plot for H₂O

Carbon

The carbon system is relatively simple compared with lithium, beryllium, or boron. There are only five major exhaust products. For high carbon atom levels and low LOX, solid carbon in the form of graphite is formed in the exhaust. At lower carbon atom levels and low LOX, methane is formed as the major exhaust product. Note that for all optimum specific impulse levels where the carbon atom concentrations are greater than 4%, either graphite or methane is formed. This is due to the low LOX concentrations needed to optimize the specific impulse at relatively low carbon atom densities. When higher amounts of LOX are added, the output products shift to CO and small amounts of CO₂. To obtain the optimum specific impulse for the carbon system at 7 mole %, no LOX is needed, there is a gain of about 120 seconds in I_{sp} (over LH₂ / LOX), and the major exhaust product is methane.

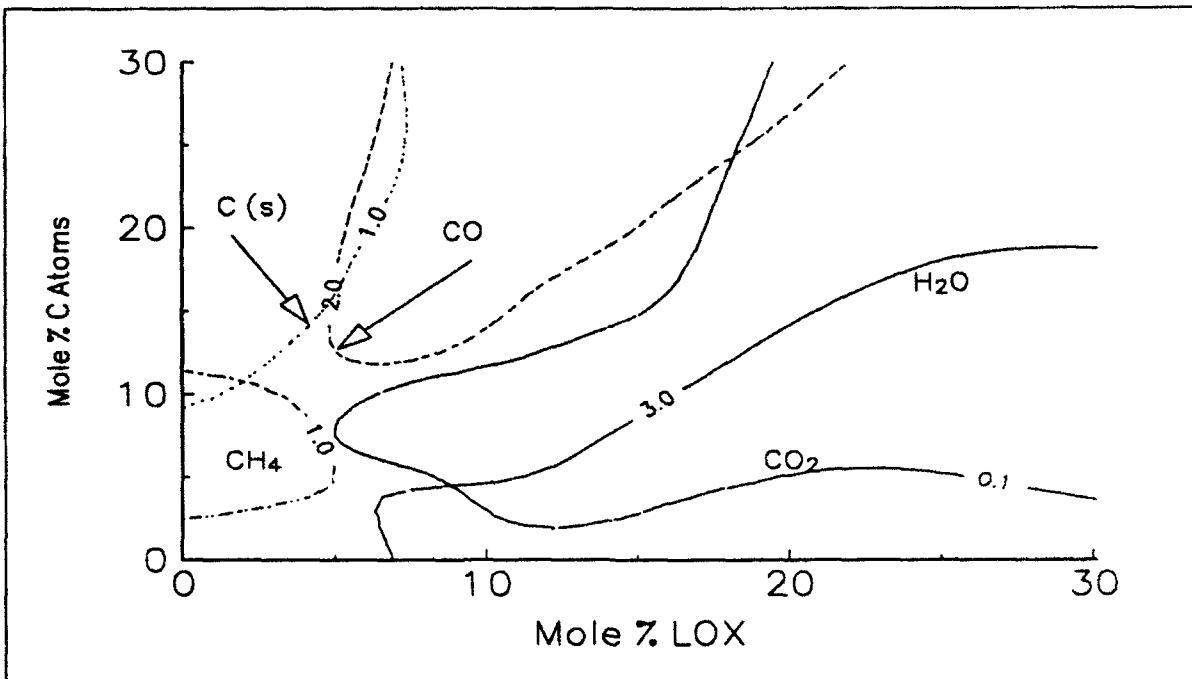


FIGURE 13a
Exhaust Product Contour Plot for Carbon

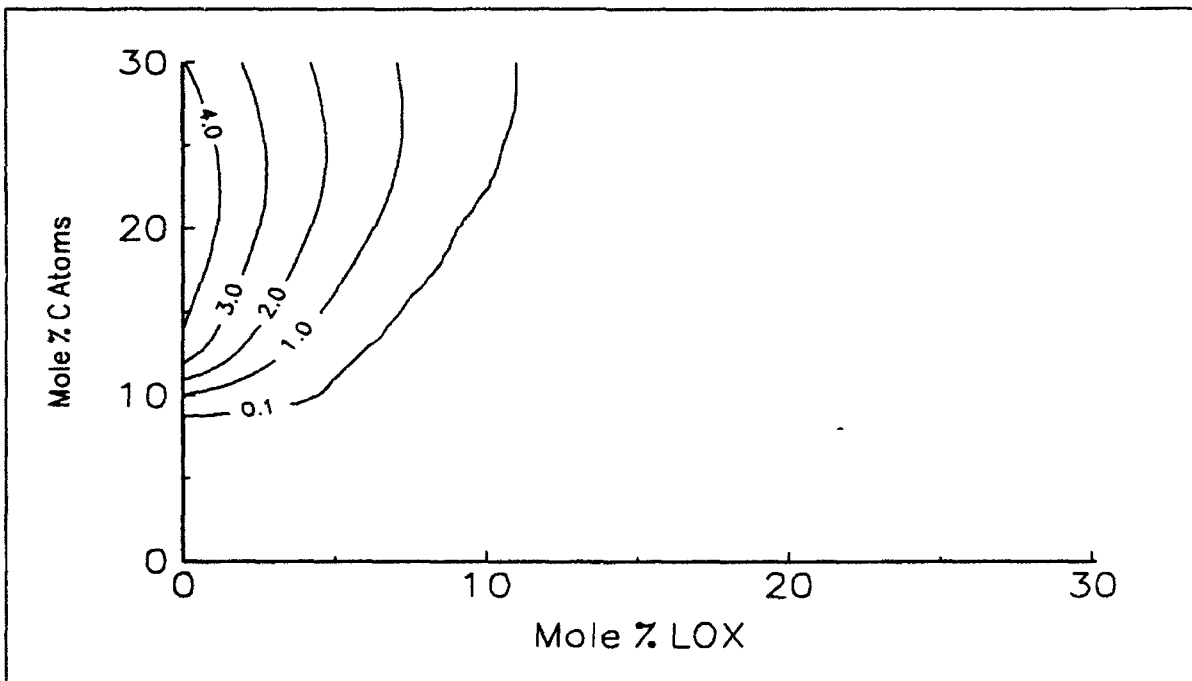


FIGURE 13b
Exhaust Product Contour Plot for C (graphite)

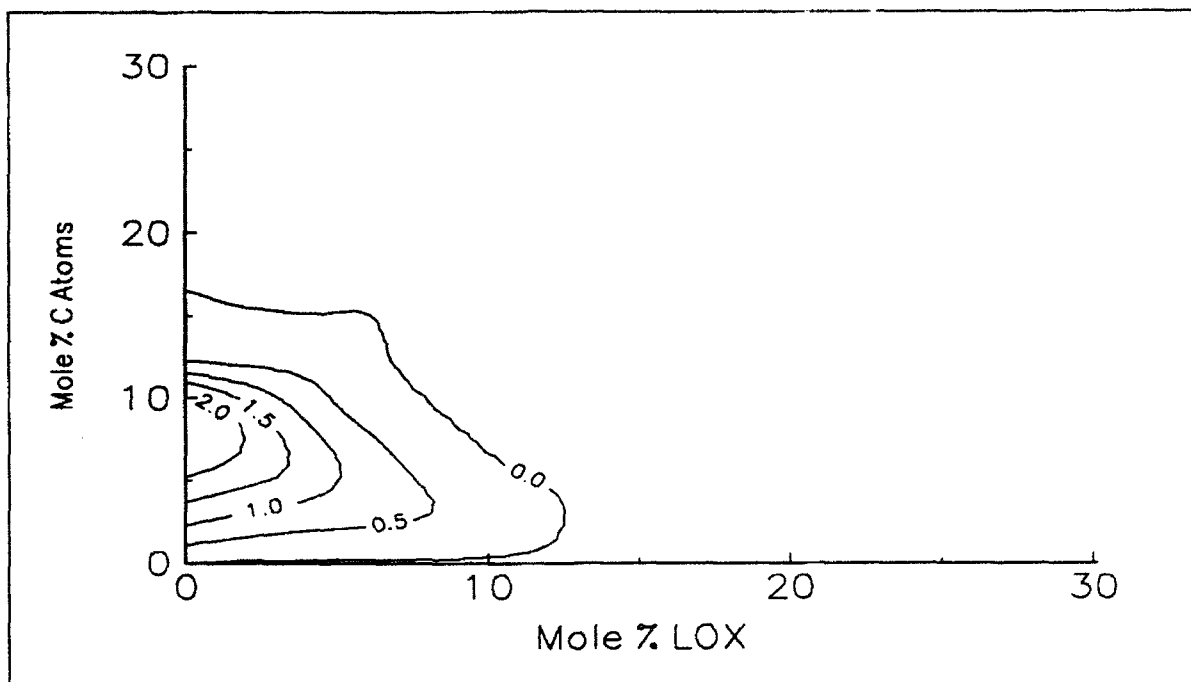


FIGURE 13c
Exhaust Product Contour Plot for CH₄

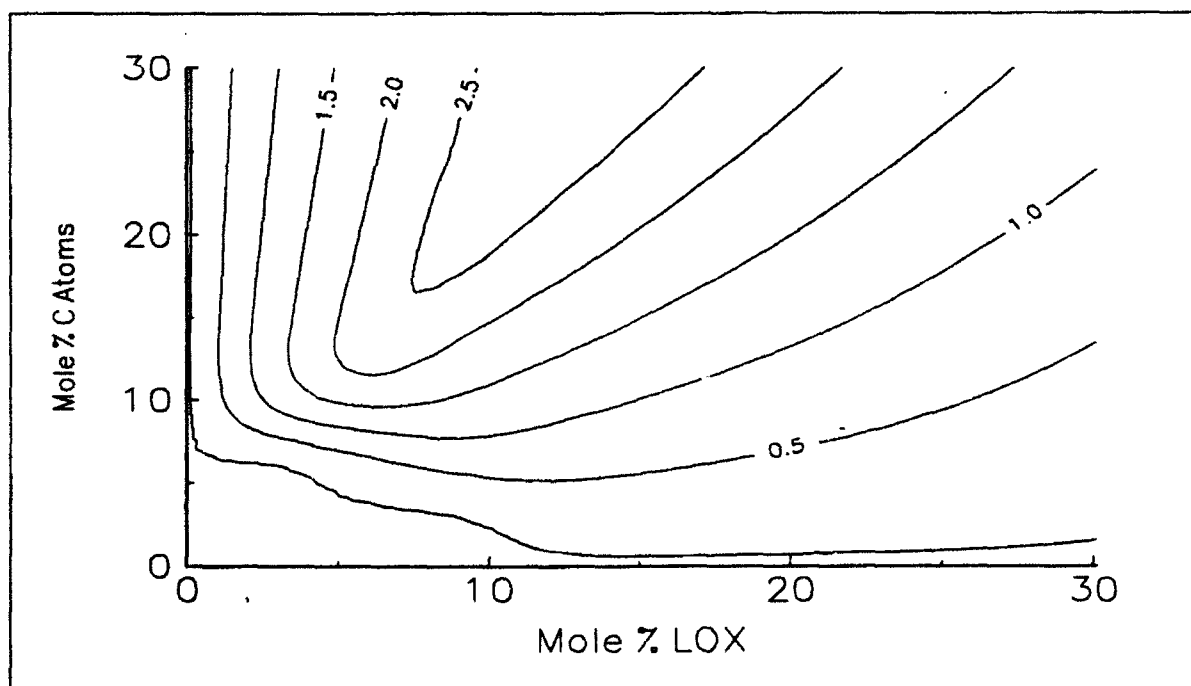


FIGURE 13d
Exhaust Product Contour Plot for CO

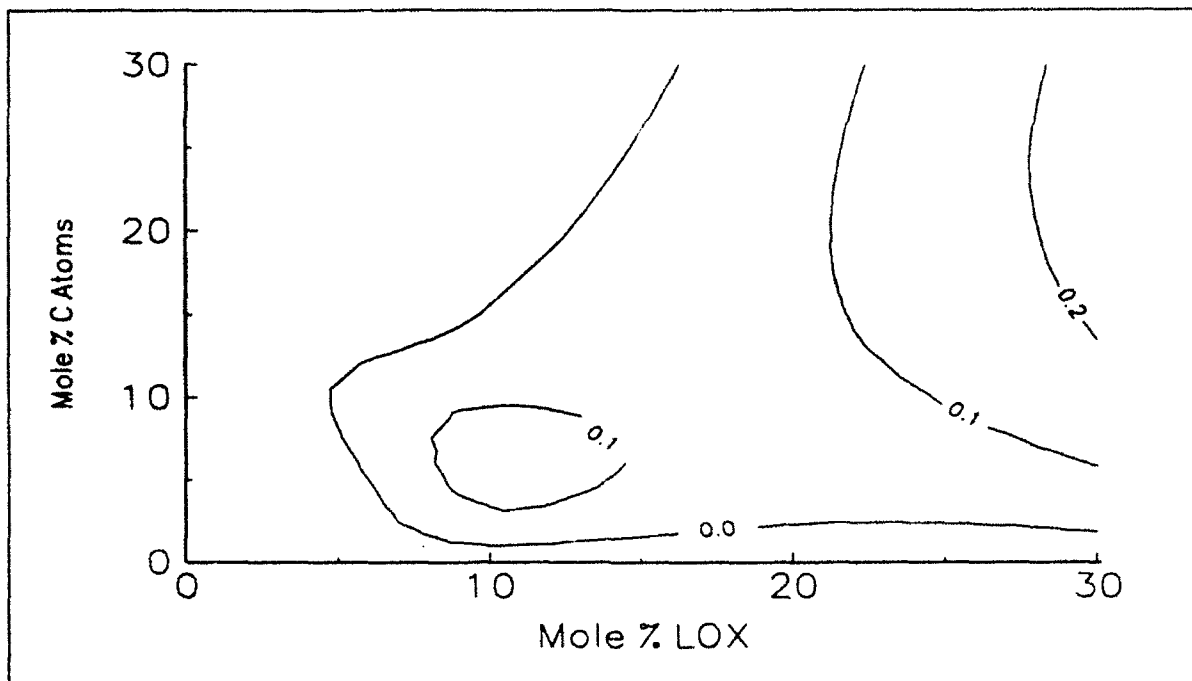


FIGURE 13e
Exhaust Product Contour Plot for CO₂

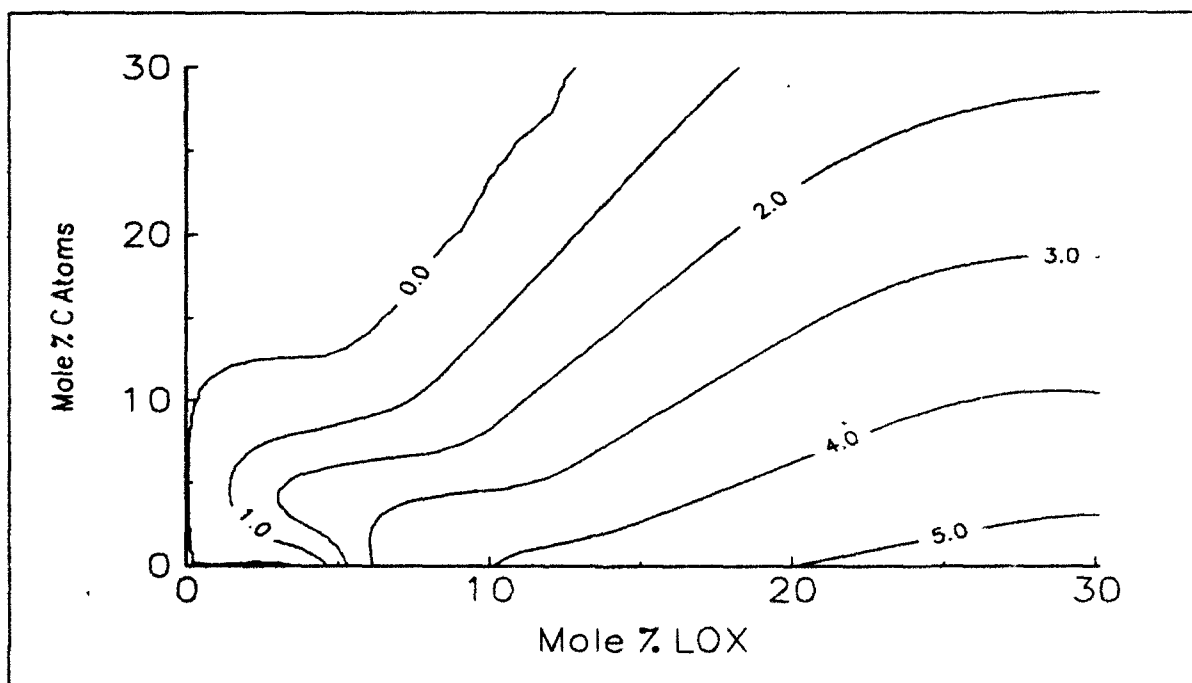


FIGURE 13f
Exhaust Product Contour Plot for H₂O

Nitrogen

The nitrogen atom in solid hydrogen system is also very simple, containing only four major exhaust products. At almost all concentration levels, the only output products are molecular nitrogen (N_2) and gaseous water. For low LOX and low nitrogen atom levels, the major product is ammonia (NH_3). Only at high N atom and high LOX levels do the products begin to shift to NO. Although nitrogen atoms give only moderate specific impulse gains at 1 to 8 mole % atoms, the clean and simple exhaust products may provide an environmentally acceptable propellant.

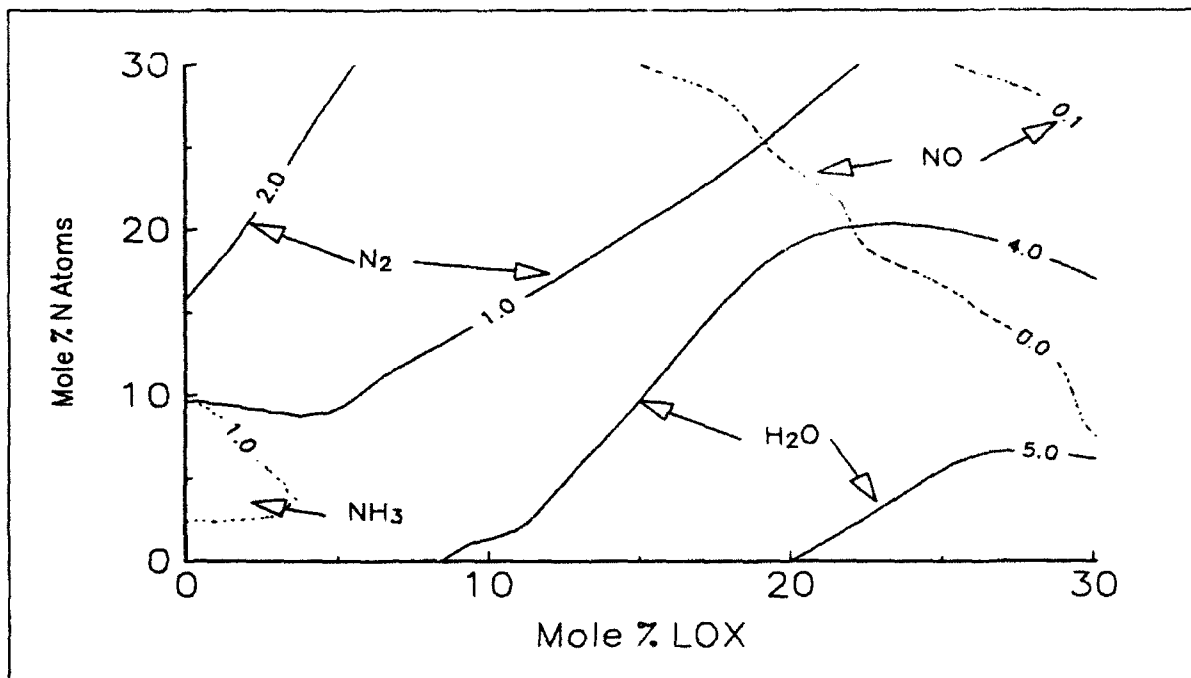


FIGURE 14a
Exhaust Product Contour Plot for Nitrogen

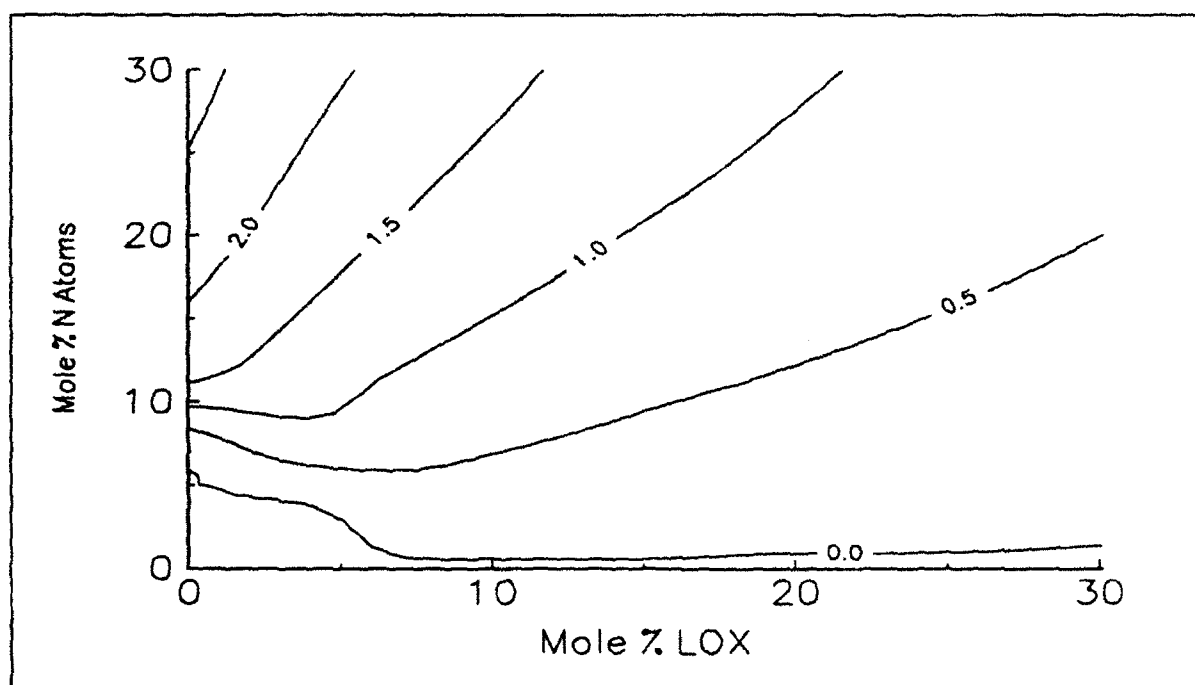


FIGURE 14b
Exhaust Product Contour Plot for N₂

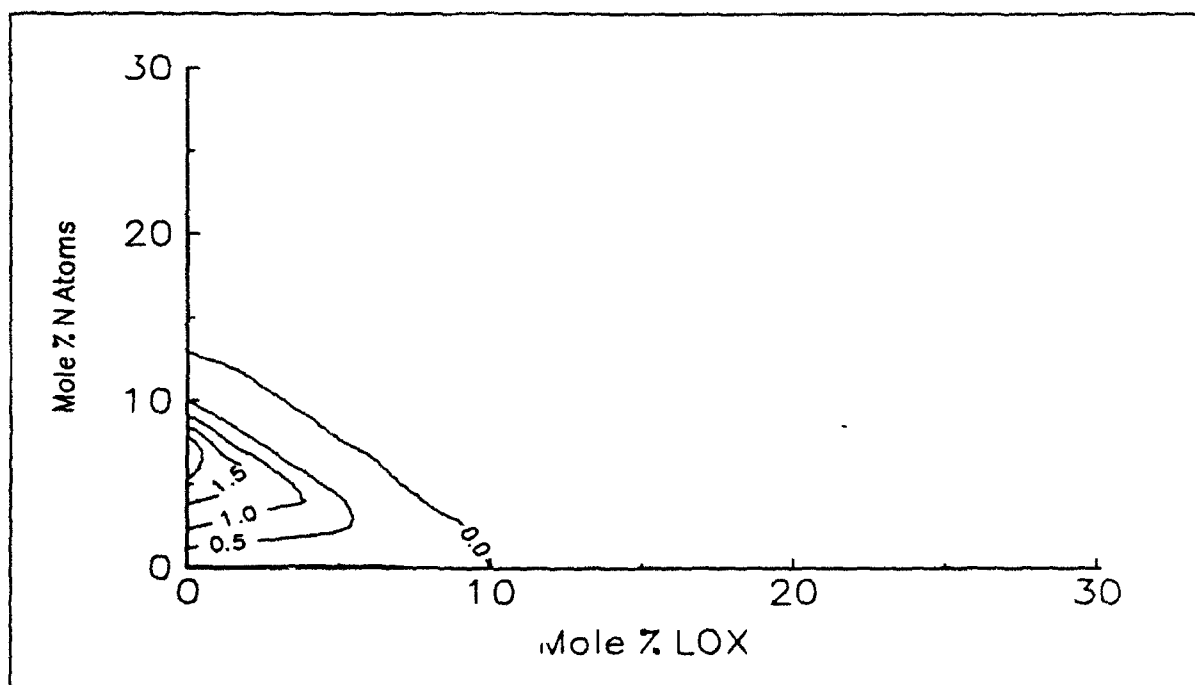


FIGURE 14c
Exhaust Product Contour Plot for NH₃

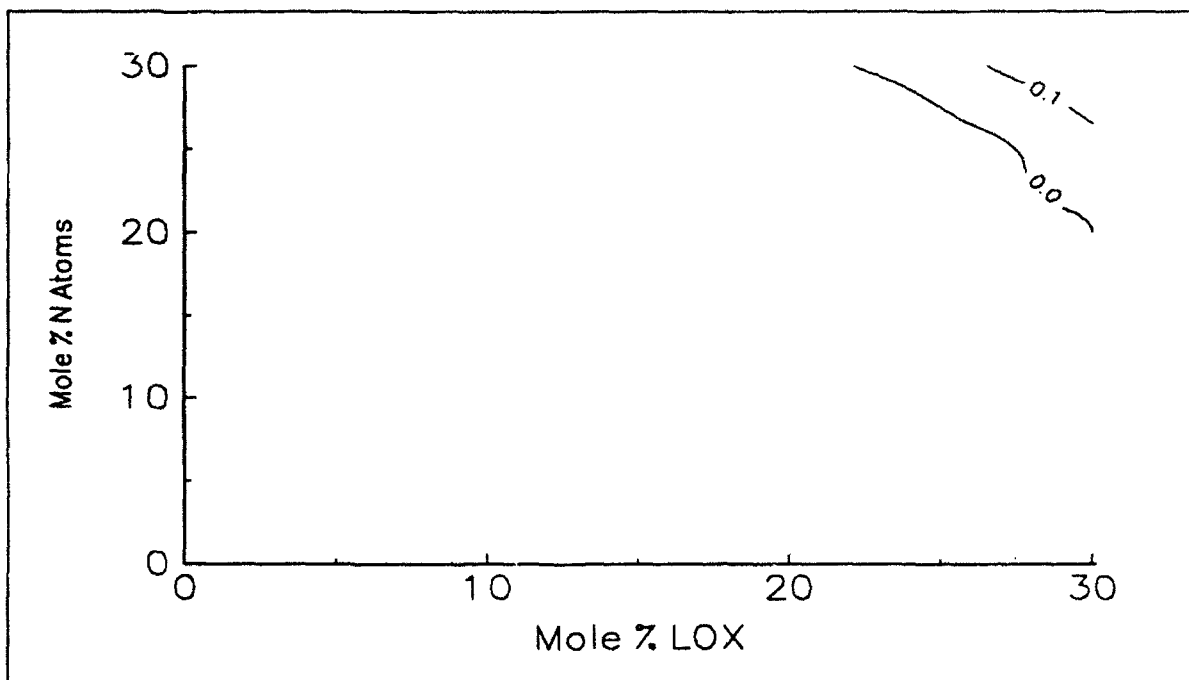


FIGURE 14d
Exhaust Product Contour Plot for NO

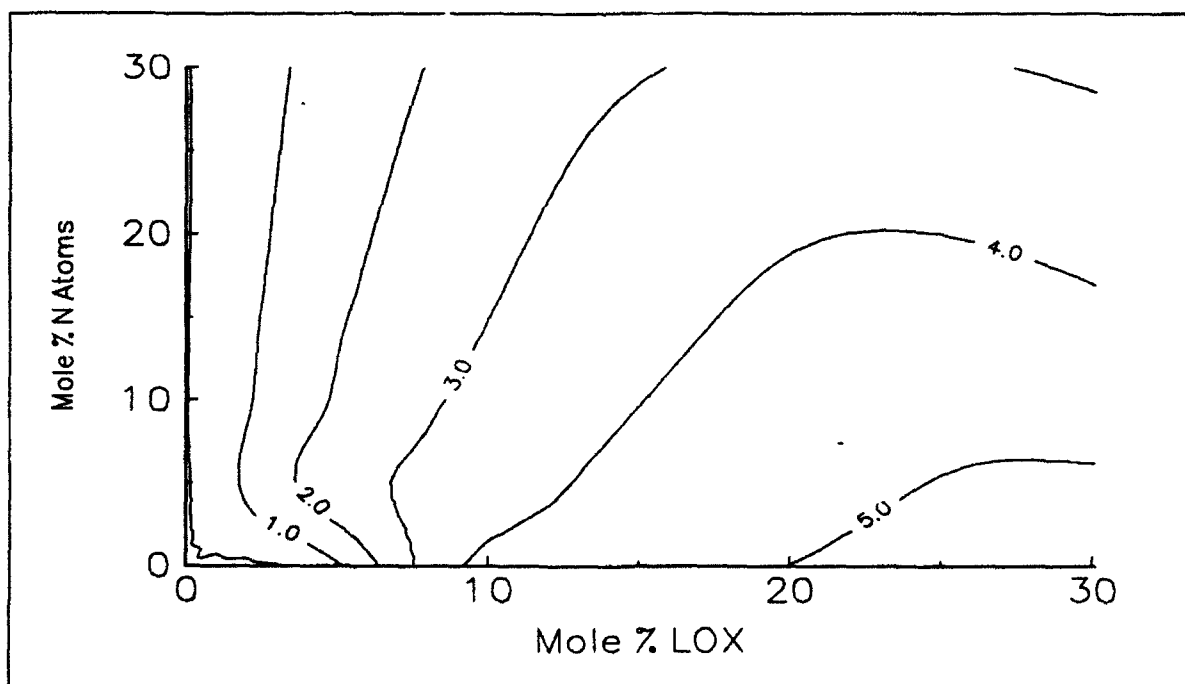


FIGURE 14e
Exhaust Product Contour Plot for H₂O

Magnesium

The magnesium system is also relatively simple. At high magnesium atom levels, the major products are unreacted magnesium atoms and liquid magnesium. For moderate magnesium atom and LOX levels, magnesium hydroxide ($\text{Mg}(\text{OH})_2$) is primarily formed in the exhaust. At all other levels, MgO (solid) is formed. Since the specific impulse gains are small for this system and due to the less desirable exhaust products, magnesium atoms in solid hydrogen is probably not a suitable system for further consideration.

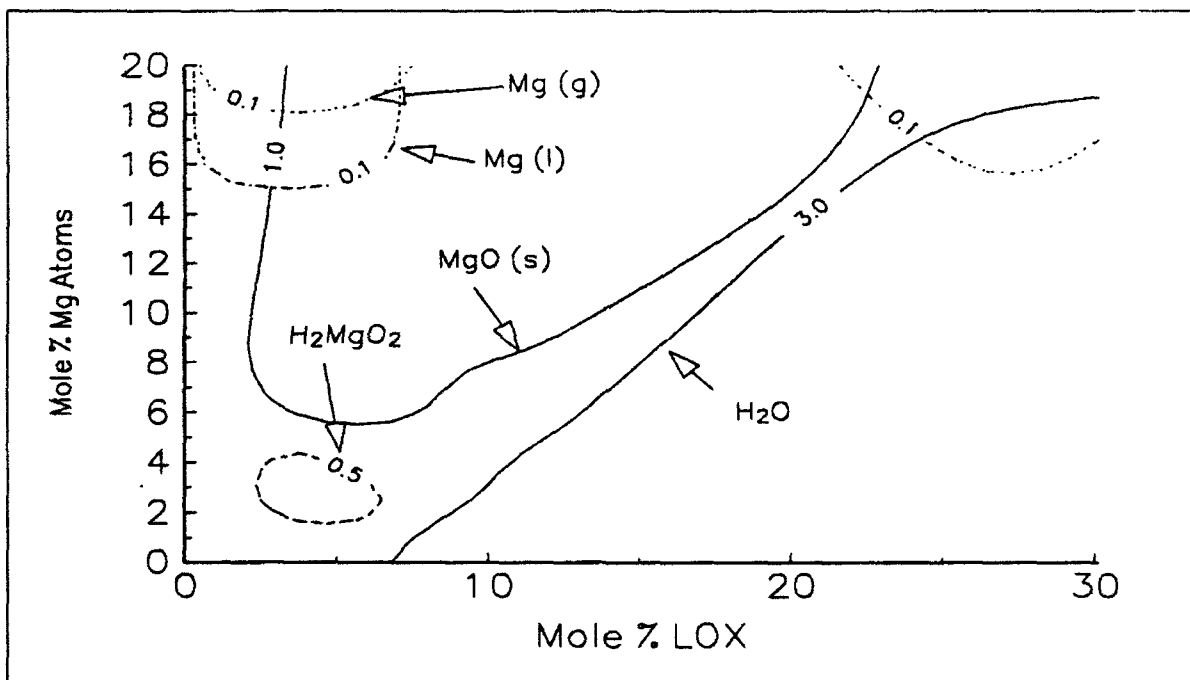


FIGURE 15a
Exhaust Product Contour Plot for Magnesium

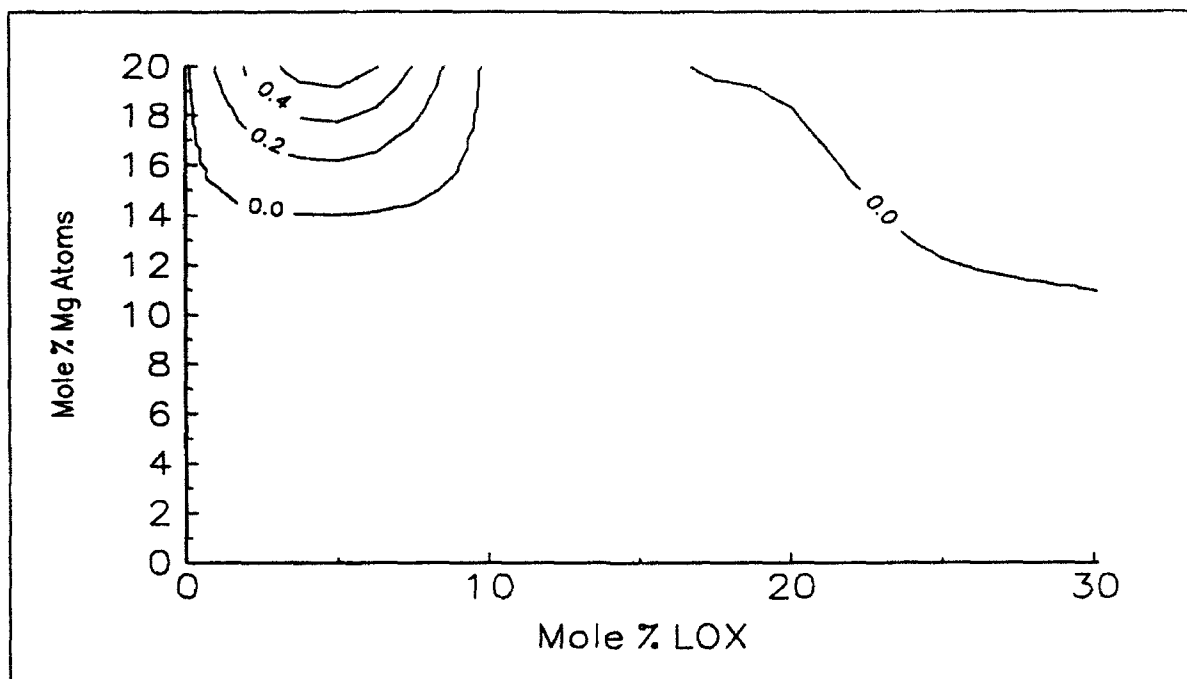


FIGURE 15b
Exhaust Product Contour Plot for Mg (g)

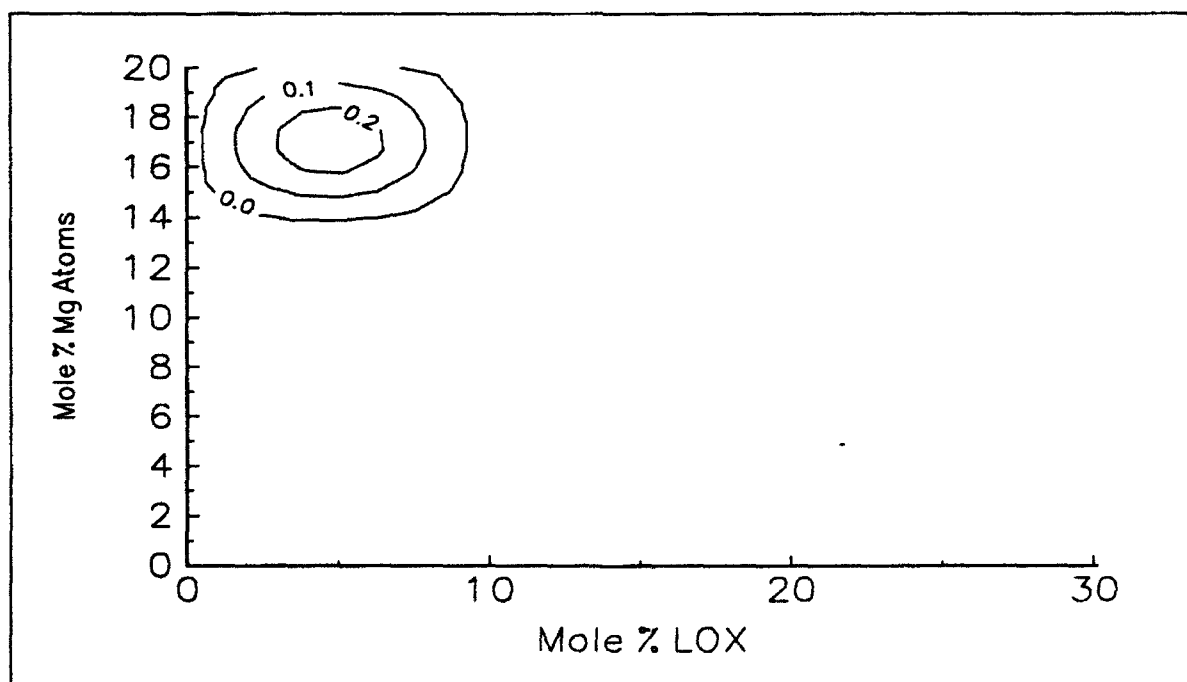


FIGURE 15c
Exhaust Product Contour Plot for Mg (l)

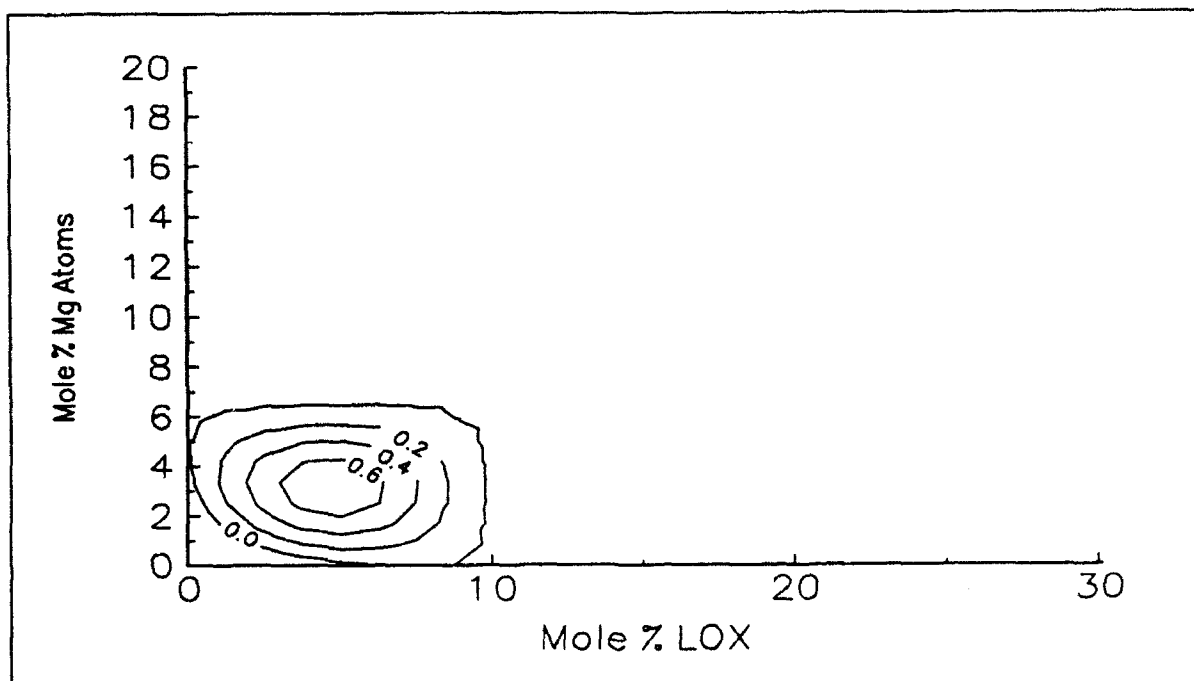


FIGURE 15d
Exhaust Product Contour Plot for H_2MgO_2 (g)

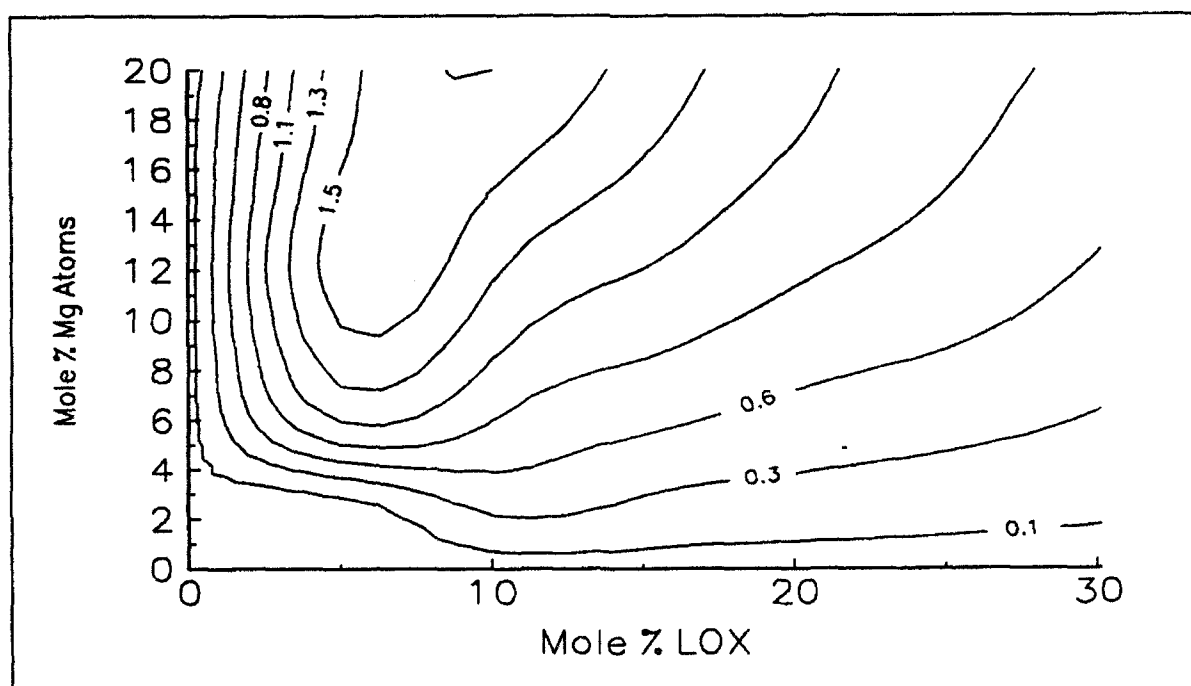


FIGURE 15e
Exhaust Product Contour Plot for MgO (s)

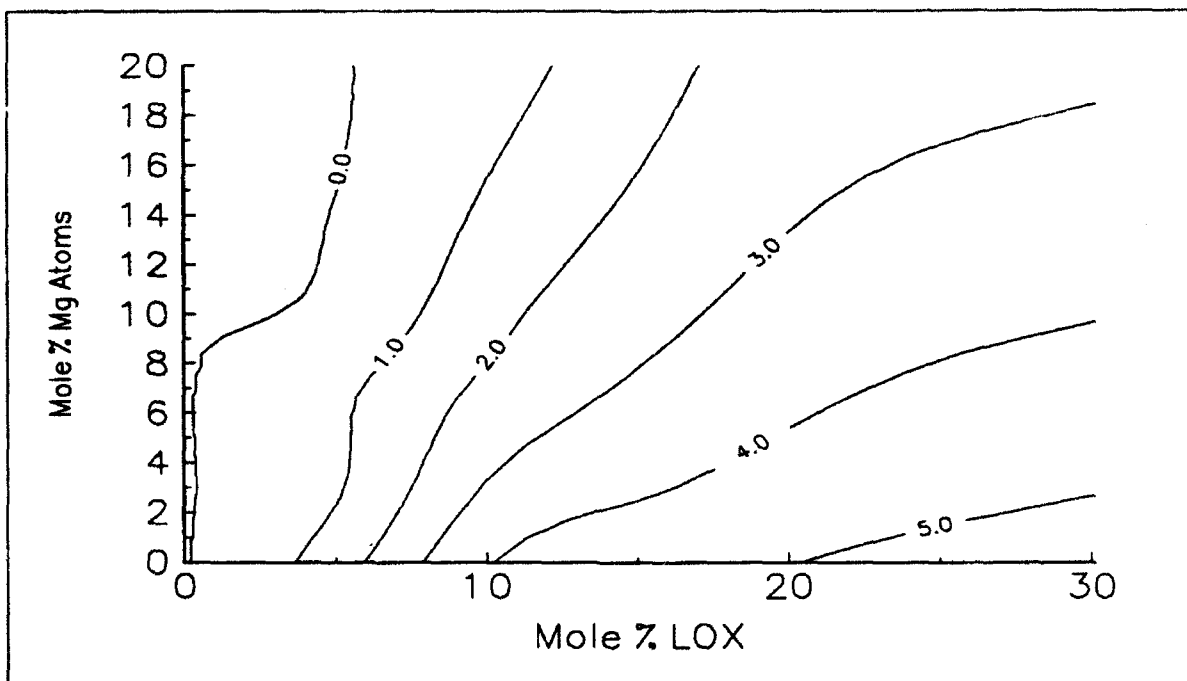


FIGURE 15f
Exhaust Product Contour Plot for H₂O

Aluminum

The aluminum system is somewhat complicated, with eight different major exhaust products. For relatively low LOX levels, aluminum liquid or solid is formed in the exhaust stream. At high aluminum atom concentrations and moderate LOX levels, both uncombusted Al and partially combusted Al_2O are the major products. When the oxidizer concentration is increased high enough or the aluminum atom level is low enough, the major product is the fully oxidized Al_2O_3 . The most interesting region is at the optimum specific impulse area, around 9 mole % Al atoms and about 7 mole % LOX. At that location, the gain in specific impulse (over LH₂ / LOX) is about 60 seconds and the major output products are solid Al_2O_3 in the alpha phase and gaseous water. If a rocket system can be designed that can withstand solid exhaust products, this may be a system worth consideration.

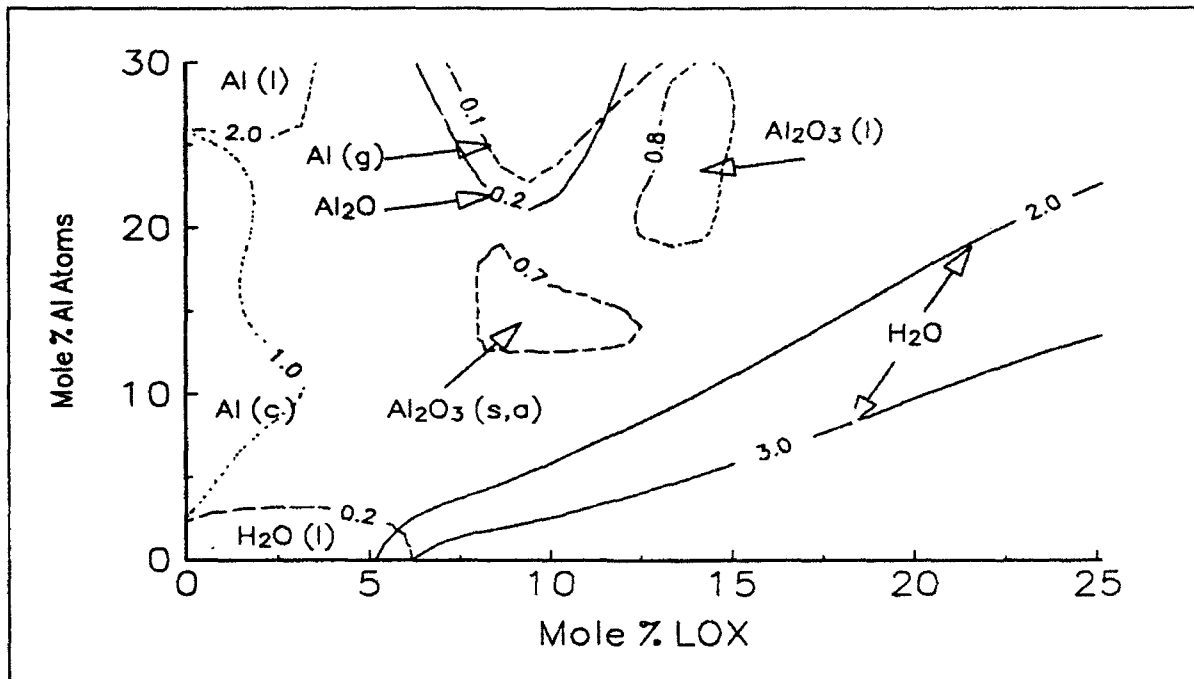


FIGURE 16a
Exhaust Product Contour Plot for Aluminum

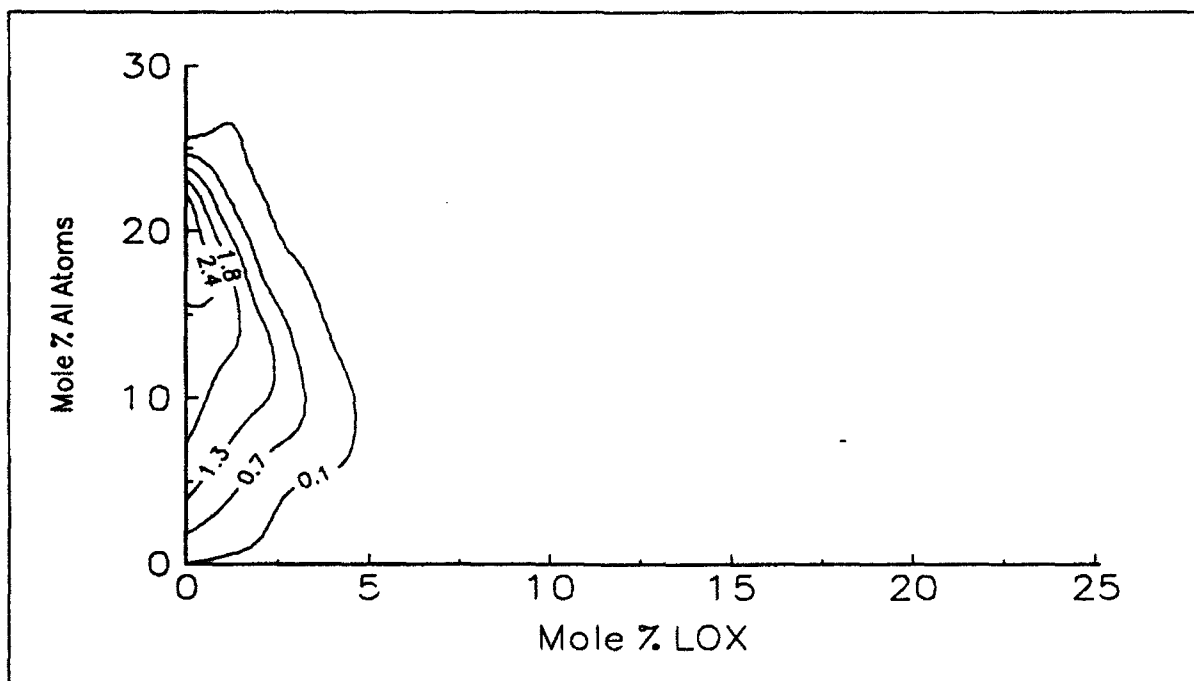


FIGURE 16b
Exhaust Product Contour Plot for Al (s)

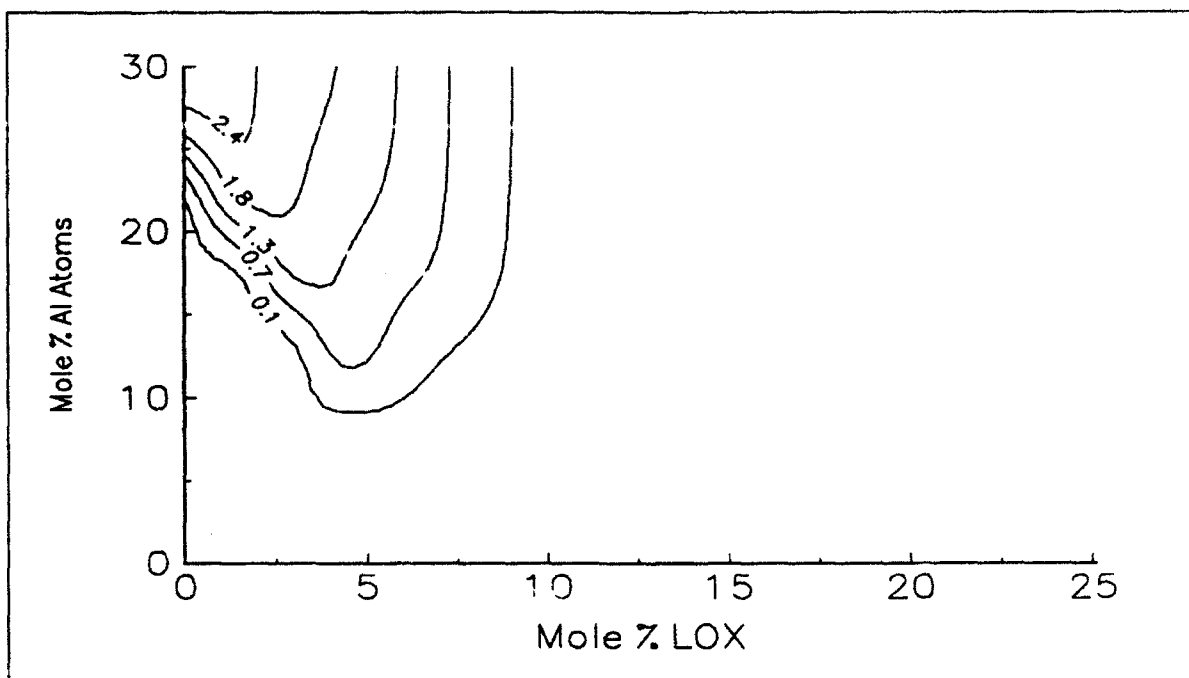


FIGURE 16c
Exhaust Product Contour Plot for Al (l)

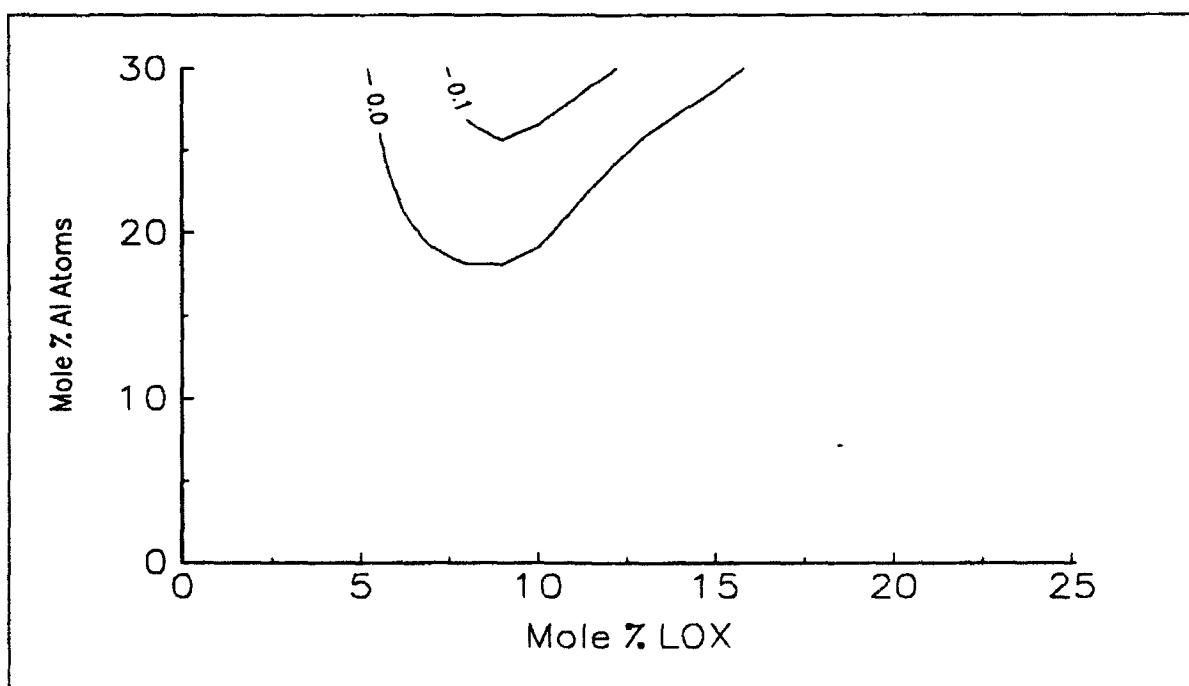


FIGURE 16d
Exhaust Product Contour Plot for Al (g)

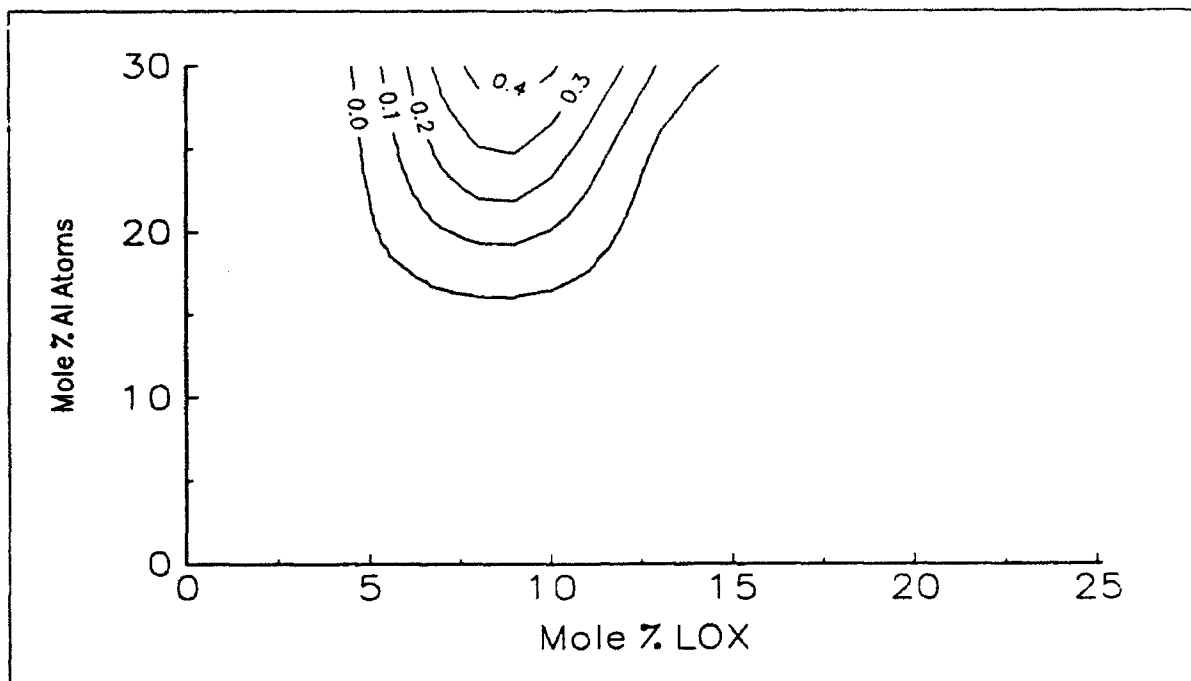


FIGURE 16e
Exhaust Product Contour Plot for $\text{Al}_2\text{O}(\text{g})$

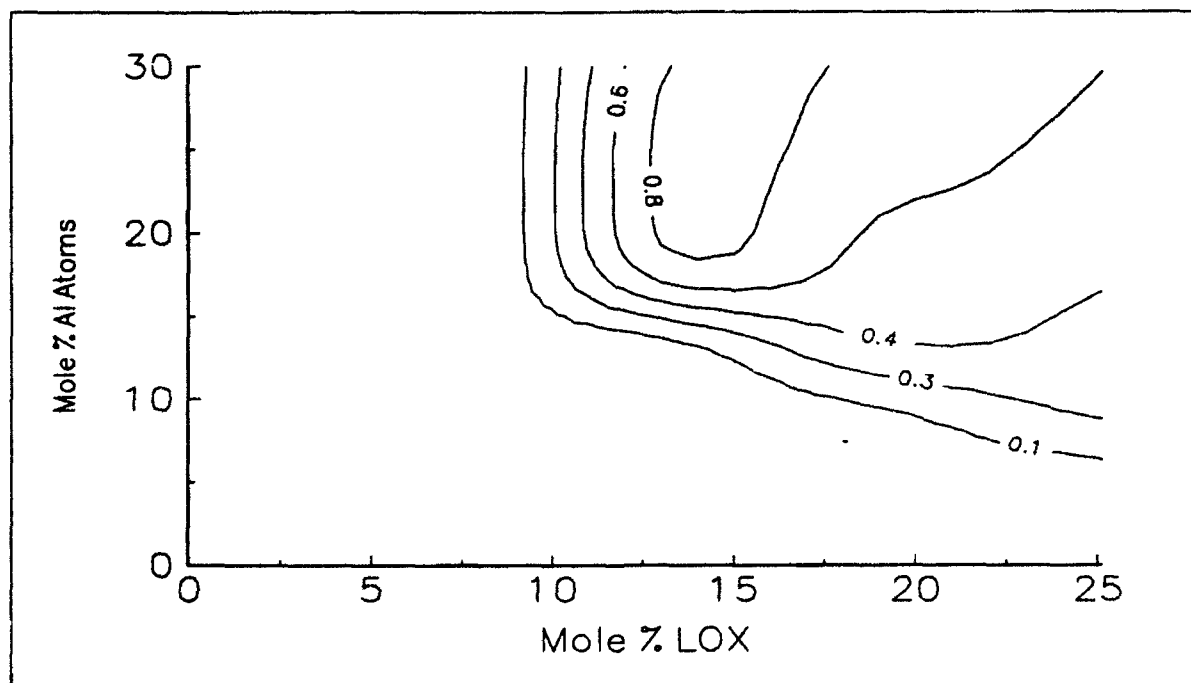


FIGURE 16f
Exhaust Product Contour Plot for $\text{Al}_2\text{O}_3(\text{l})$

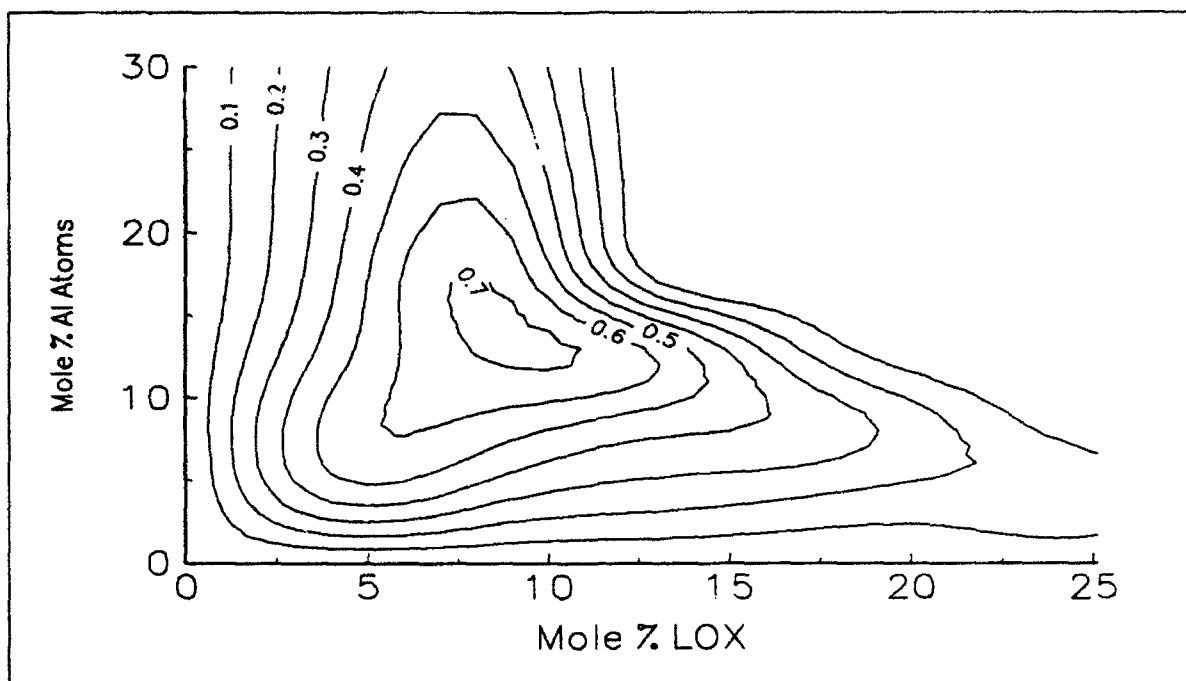


FIGURE 16g
Exhaust Product Contour Plot for Al_2O_3 (s,a)

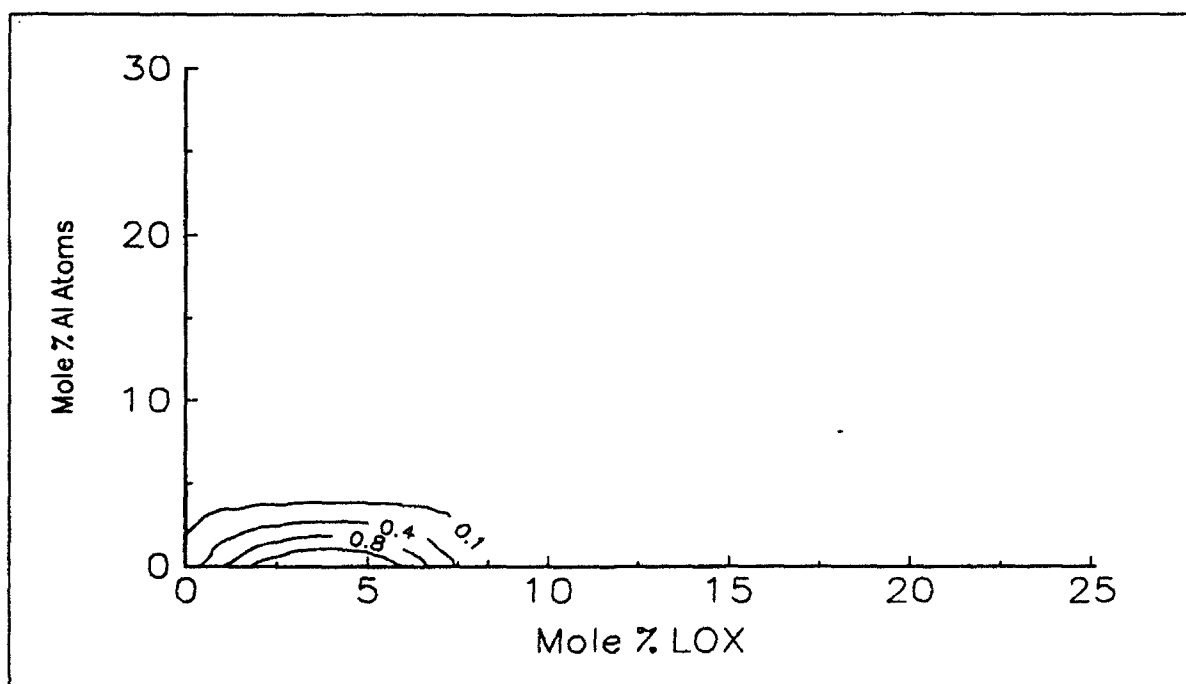


FIGURE 16h
Exhaust Product Contour Plot for H_2O (l)

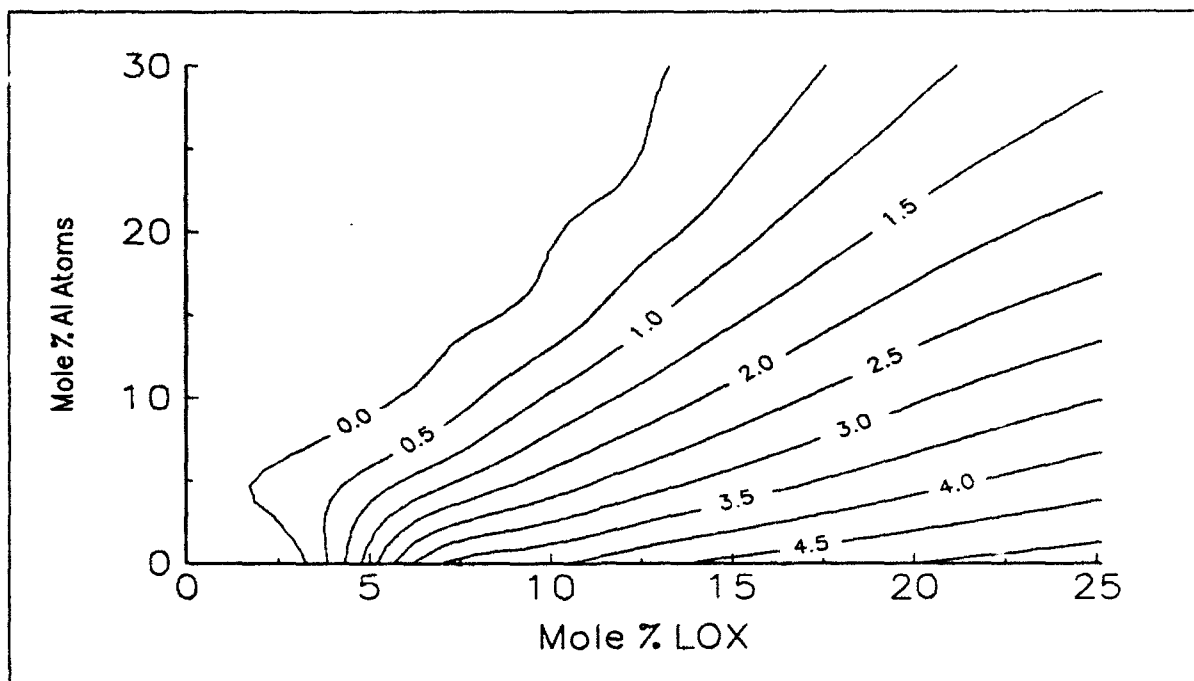


FIGURE 16i
Exhaust Product Contour Plot for H₂O

EXHAUST PRODUCTS FOR FIXED 5 MOLE PERCENT ATOMS IN SOLID HYDROGEN

The above contour plots of the output products shows complicated patterns that can be simplified by taking "cuts" of the concentrations of all the important species at a given concentration of additive. Cuts at 5 mole percent of these atoms in solid hydrogen show the important output products and are given in Figures 17 through 24. The top graph in each plot shows the temperature in the chamber and the optimized specific impulse for liquid oxygen concentrations from 0 to 30 mole percent. The bottom graph shows the cuts for the major exhaust products for the same LOX concentrations.

From these two plots, the variations in the chamber temperature and the specific impulse can be linked to the changes in the exhaust species. In each case, a change in the major exhaust species is usually accompanied by a variation in the increase in the chamber temperature. For example, in Figure 18 (showing 5% lithium in solid hydrogen), small changes in the increase in the chamber pressure can be seen for most of the changes in the major exhaust species, such as the change from LiOH gas to LiOH liquid over the 7 to 8 mole % LOX range.

The major exhaust species for the maximum specific impulse under these conditions can also be determined from a comparison of the top and bottom plots. For example, in Figure 24 (showing 5% aluminum in solid hydrogen) the maximum specific impulse corresponds to about 425 seconds and the major exhaust product at that I_{sp} value is Al_2O_3 liquid at 4 mole % LOX.

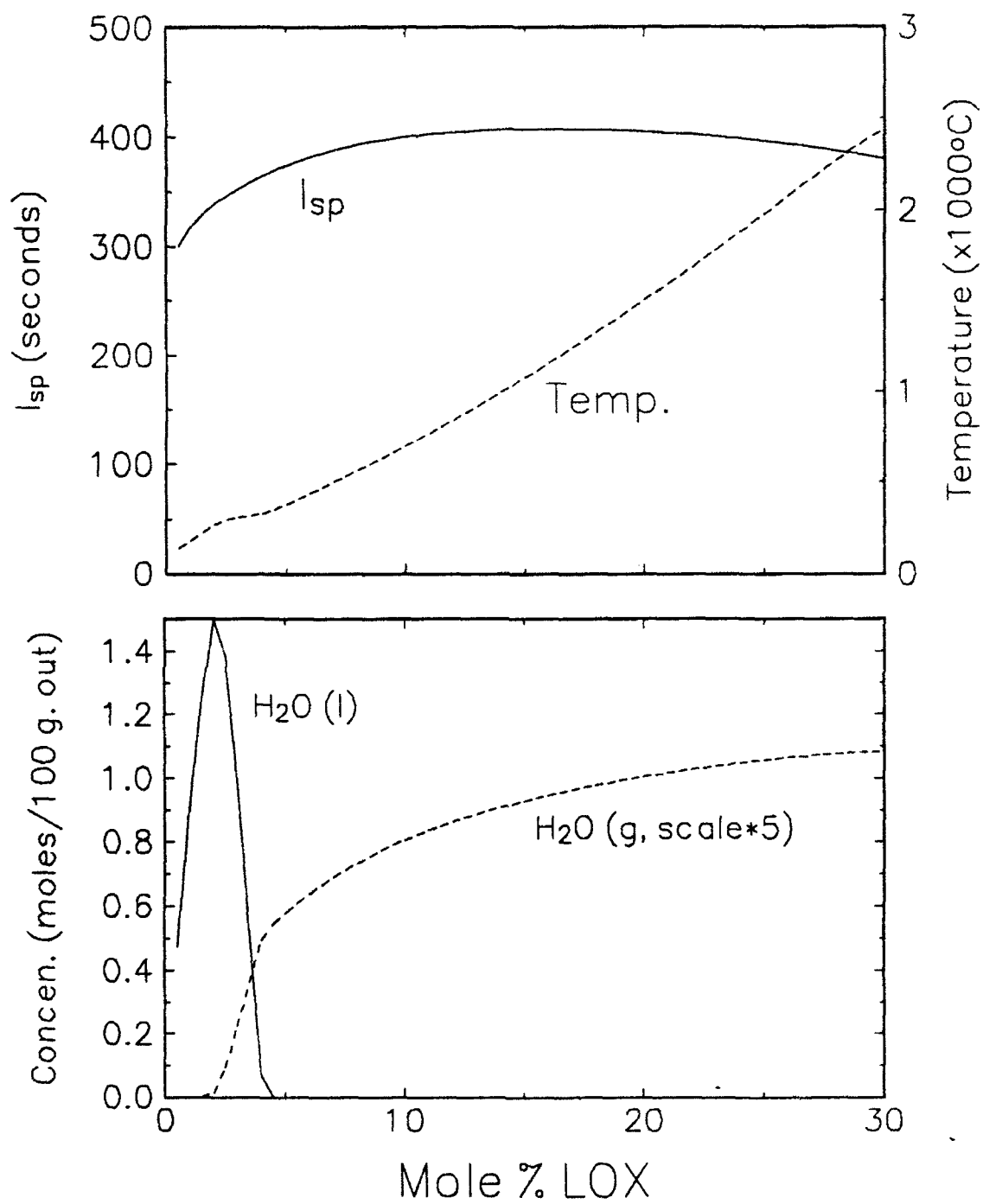


FIGURE 17
Fixed 5% Concentration Plot for Hydrogen Atoms in Solid H_2

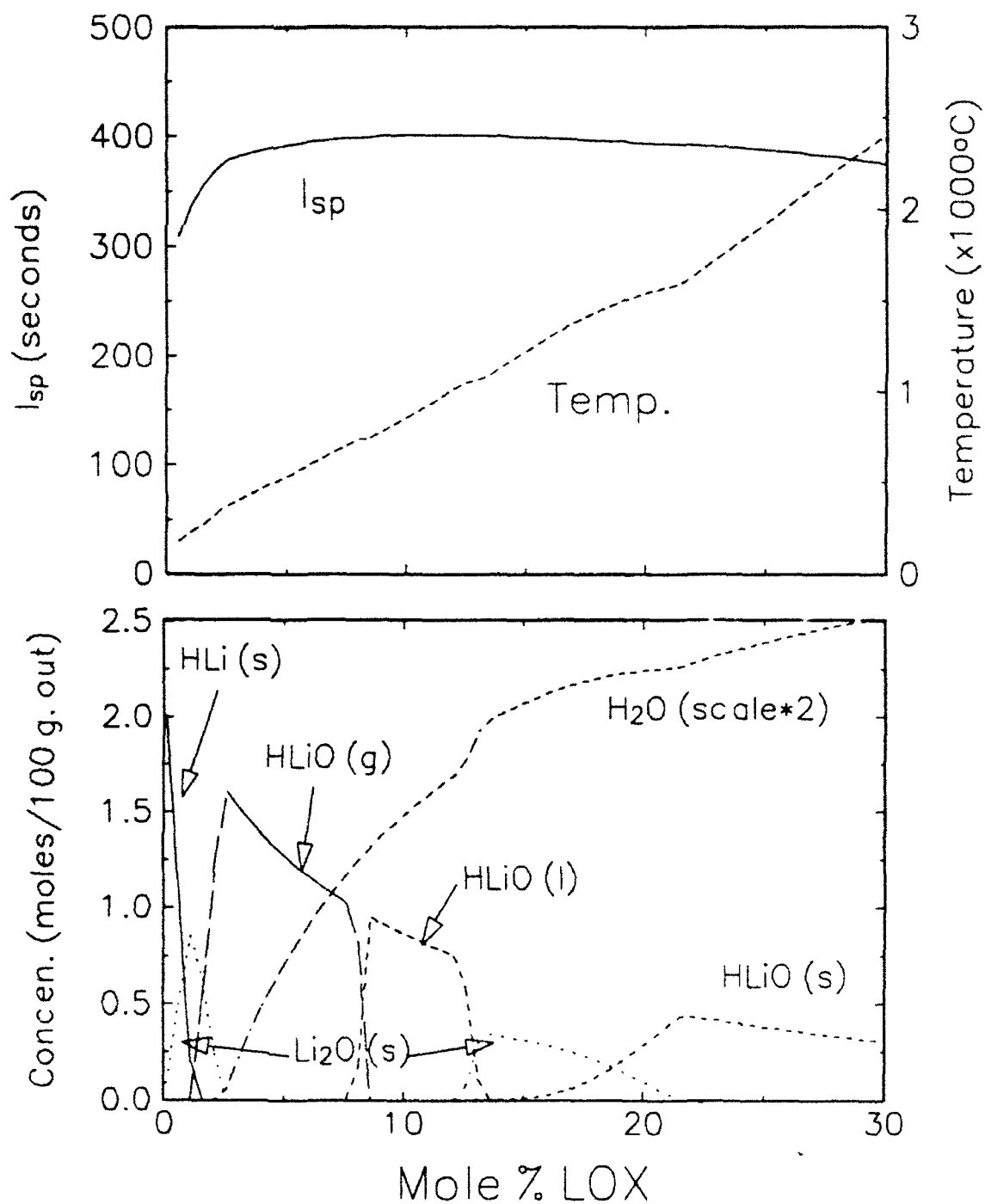


FIGURE 18
Fixed 5% Concentration Plot for Lithium Atoms in Solid H_2

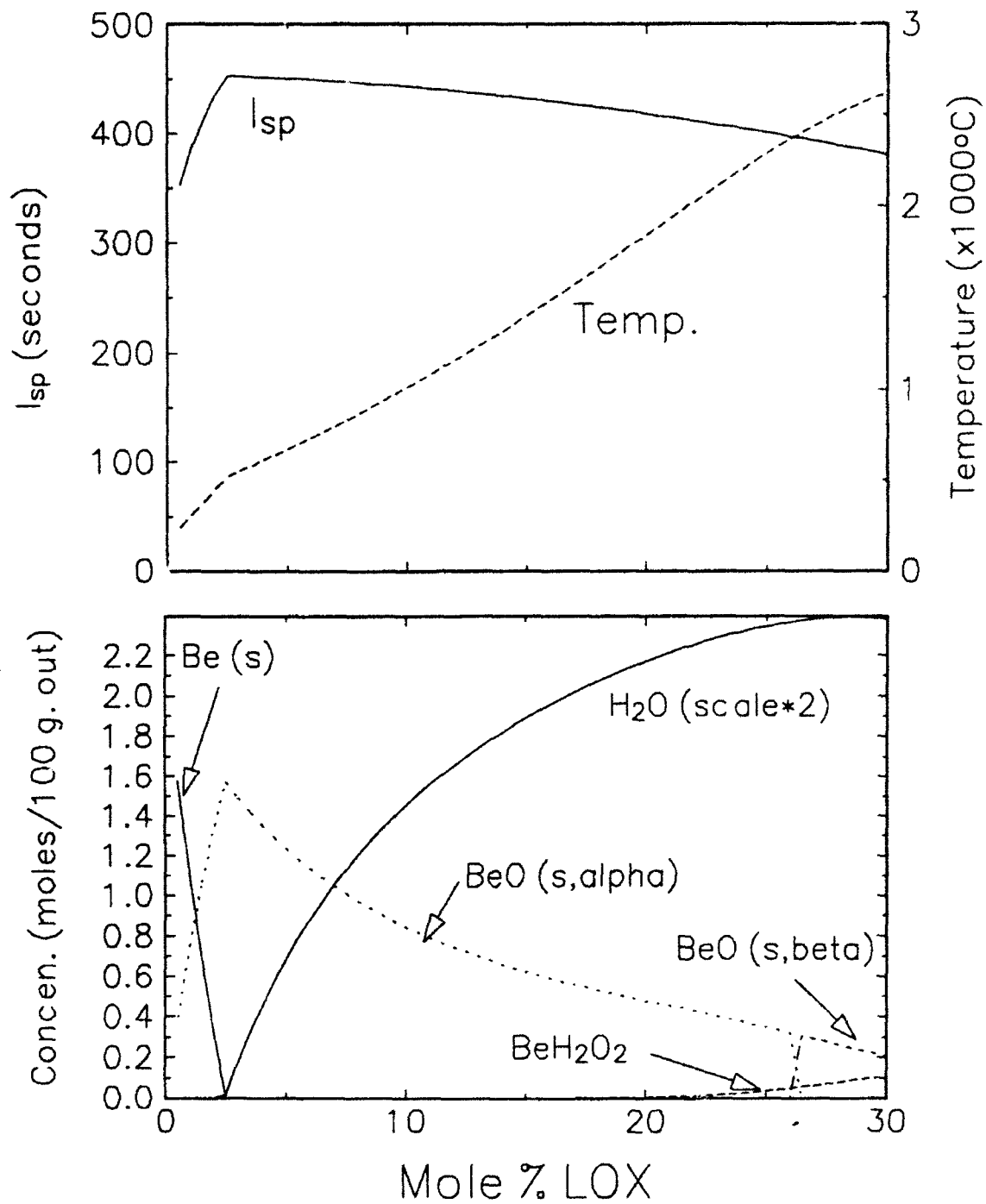


FIGURE 19
Fixed 5% Concentration Plot for Beryllium Atoms in Solid H_2

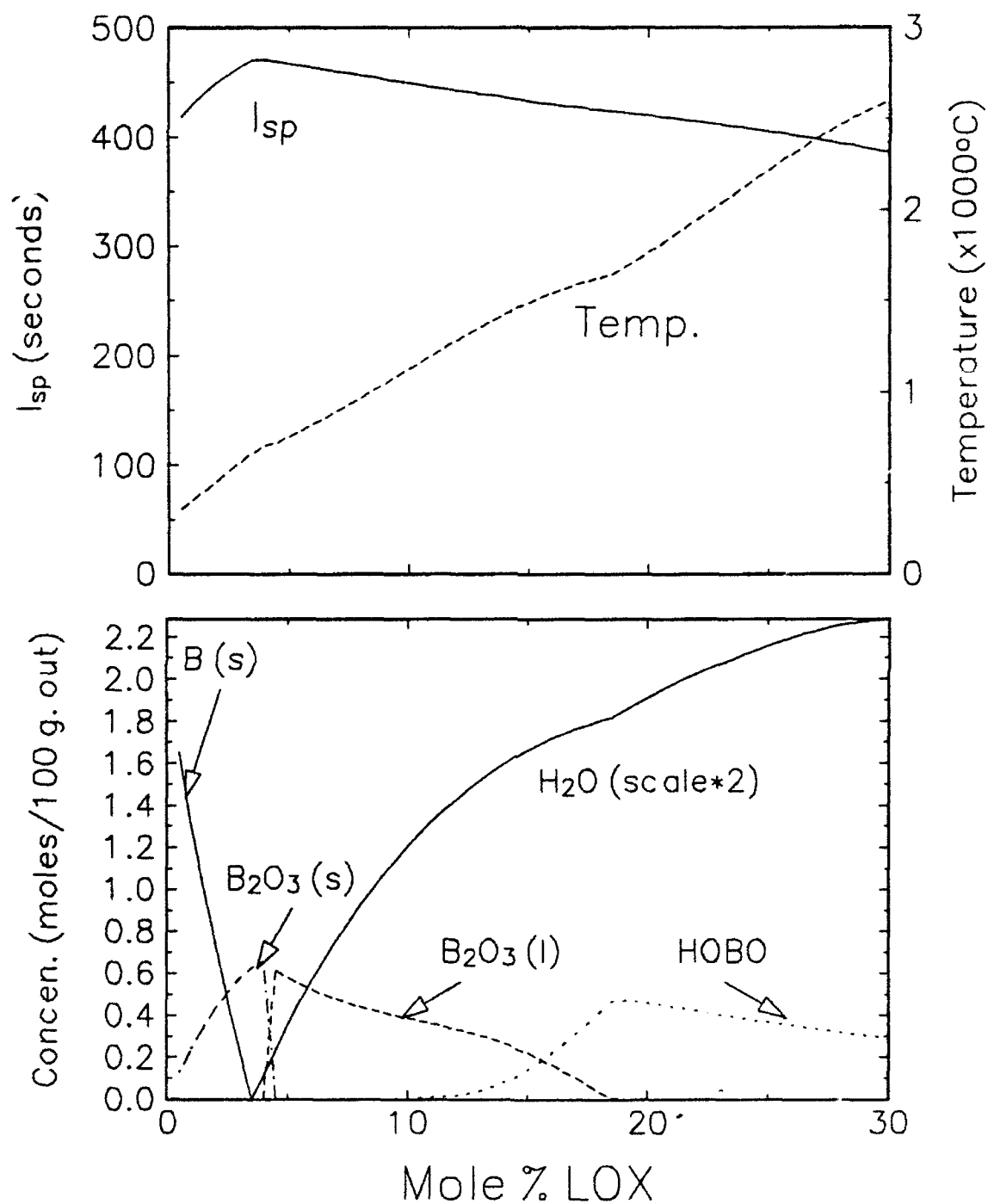


FIGURE 20
Fixed 5% Concentration Plot for Boron Atoms in Solid H_2

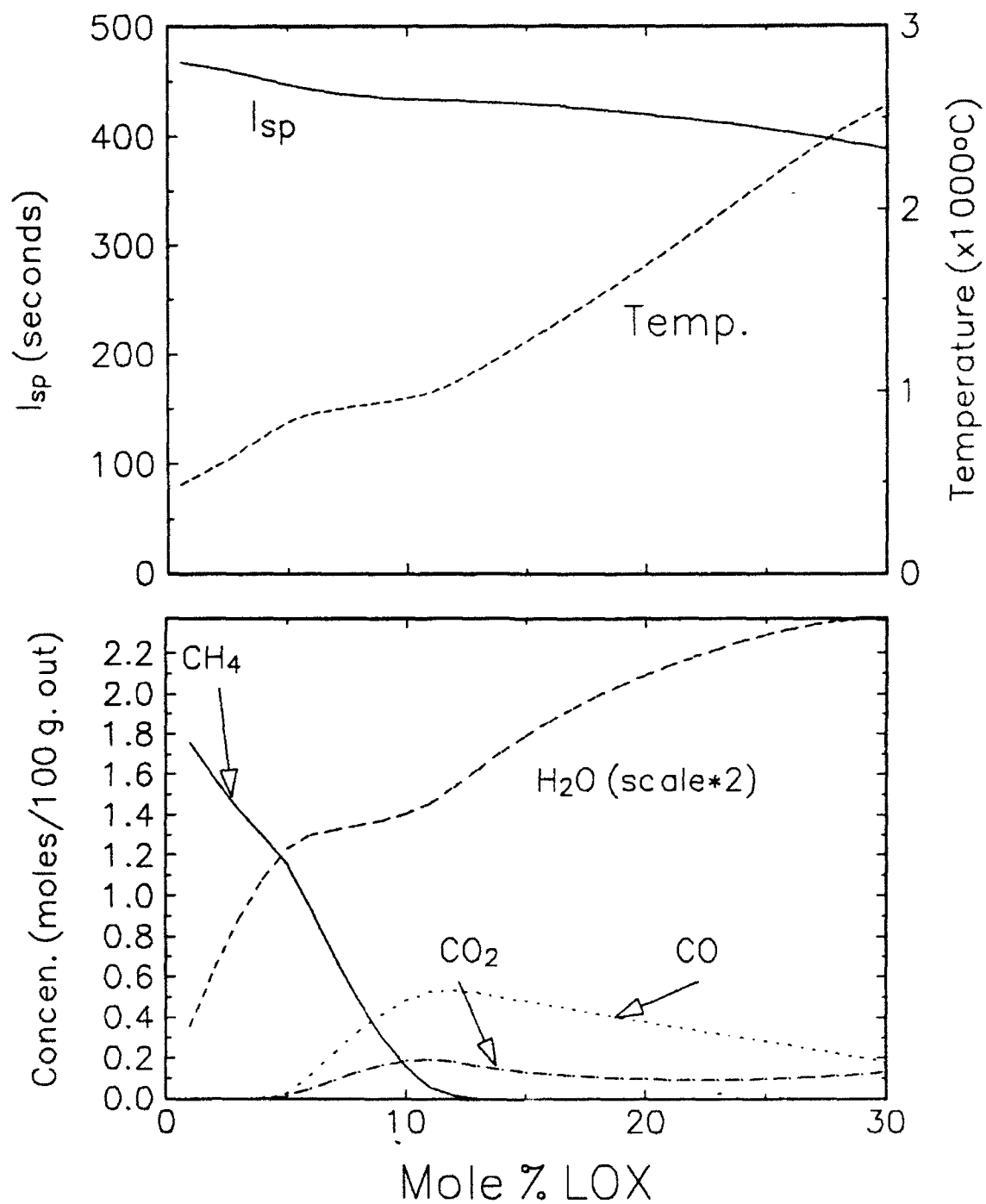


FIGURE 21
Fixed 5% Concentration Plot for Carbon Atoms in Solid H_2

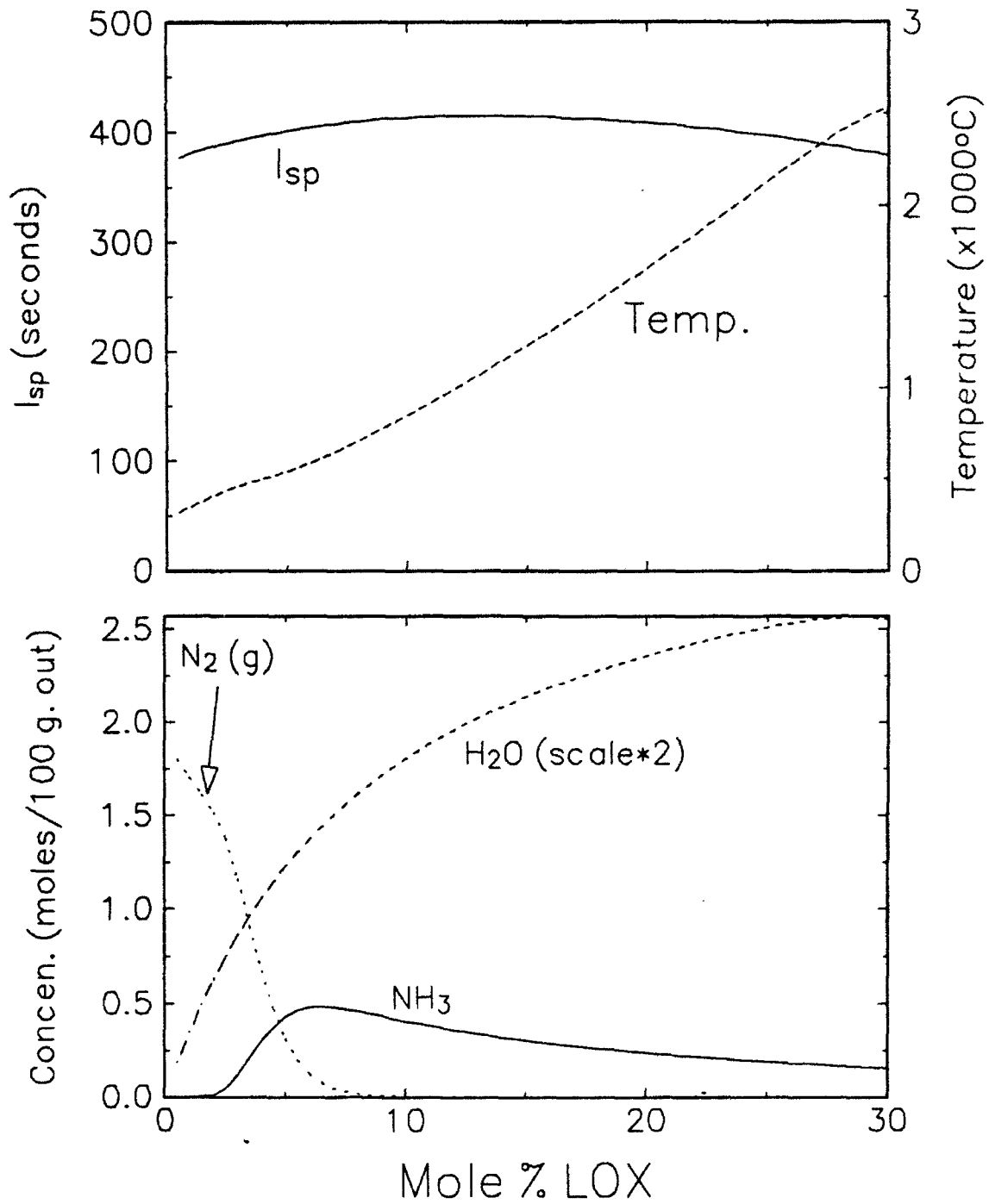


FIGURE 22
Fixed 5% Concentration Plot for Nitrogen Atoms in Solid H_2

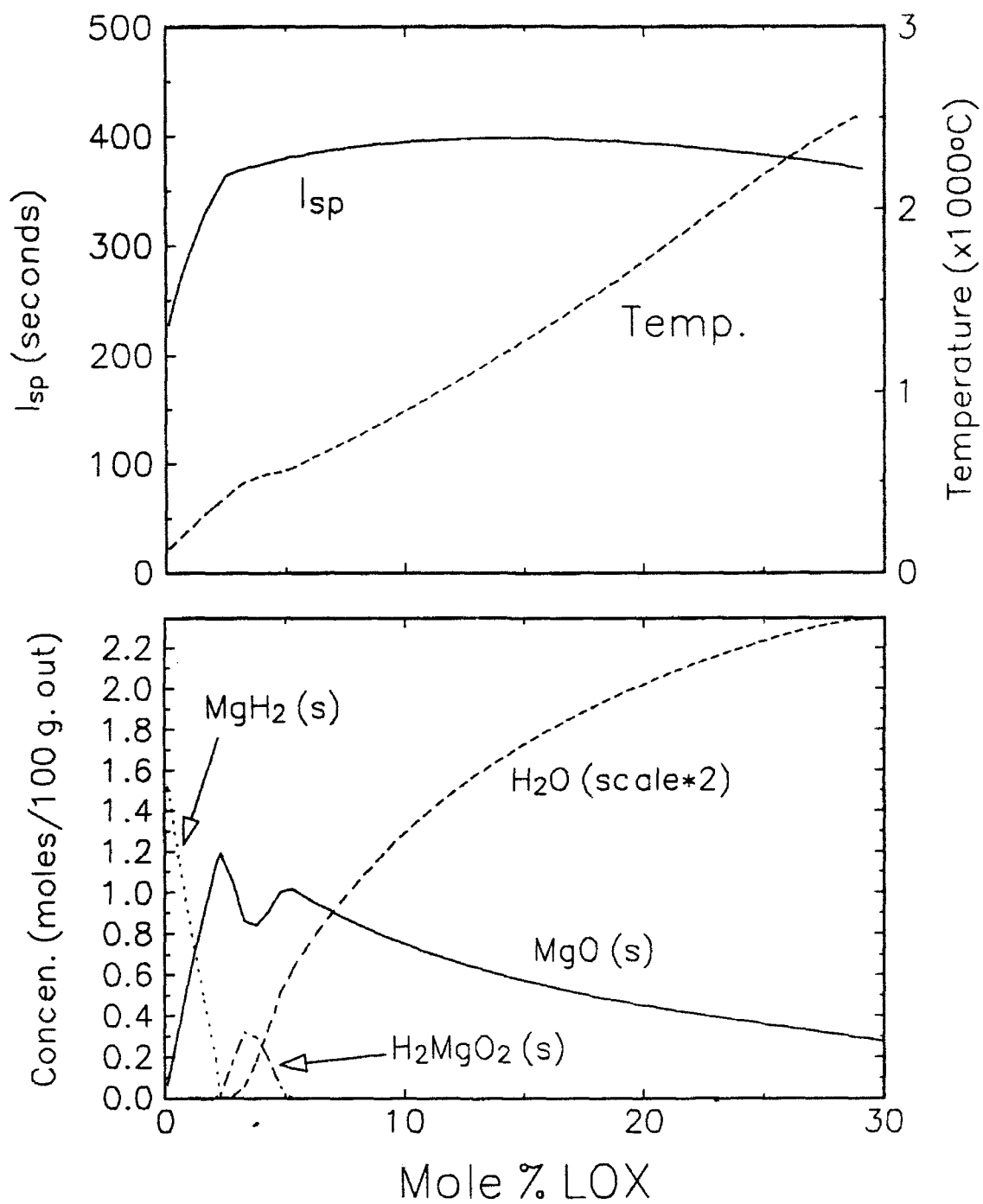


FIGURE 23
Fixed 5% Concentration Plot for Magnesium Atoms in Solid H_2

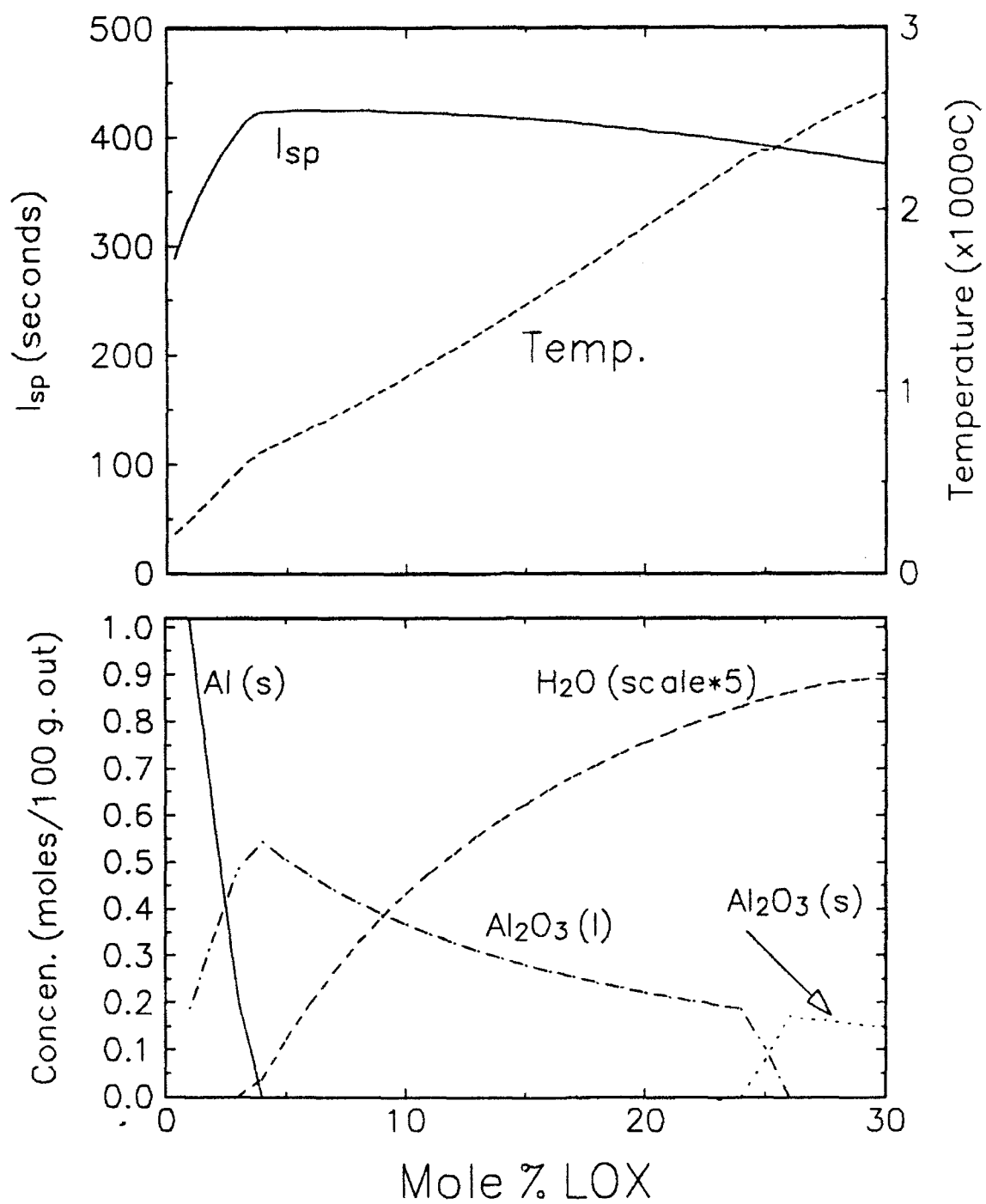


FIGURE 24
Fixed 5% Concentration Plot for Aluminum Atoms in Solid H_2

CONCLUSIONS

The specific impulse and exhaust product contours presented above can be useful for determining which atomic systems in solid cryogenic hydrogen may be of the greatest benefit. From this data it can be concluded that the atomic hydrogen, lithium, and magnesium systems are probably not of great interest. The beryllium system is also probably not of great interest, unless the extreme toxicity problems can be overcome, possibly by limiting use to only deep space applications. Of the remaining atomic systems, nitrogen and aluminum result in moderate specific impulse gains at the 5 mole percent level, although they may be of interest because of the relatively environmentally "clean" exhaust products. The boron system gives the greatest gains in I_{sp} , but the exhaust products may be somewhat undesirable and there remains the problem of H₂O formation due to kinetics (13). The carbon system has perhaps the greatest potential, giving substantial gains for fairly low atom concentrations and fairly "clean" exhaust products.

For any real system of atoms trapped in cryogenic solid hydrogen, additional trapped species have to be considered in any performance estimates. For example, energetic deposition of atoms into solid hydrogen surfaces will also produce a variety of molecular species, some of which could substantially reduce the specific impulse, while others could actually increase the performance levels. Details of the effects of small molecular species on the specific impulse will be examined in the next report in this series.

There are many basic and technical problems to the use of atomic additives to solid hydrogen propellants. There is a continuing effort in the HEDM program to explore the technology necessary to implement these exotic propellants. Many of these problems have been addressed in References 1, 9, 10 and 12. If these difficulties can be overcome, the benefits are great - increased payload to orbit, large cost savings, single-stage-to-orbit capability, and potential simplification of launch systems.

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